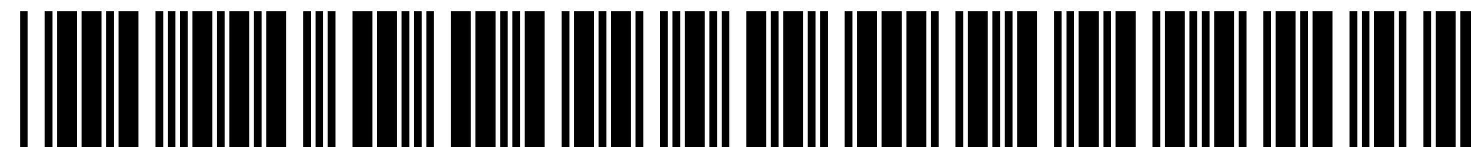

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Yonemura et al.

(10) **Patent No.: US 9,147,829 B2**
(45) **Date of Patent: *Sep. 29, 2015**

(54) **LIQUID EJECTION HEAD**

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(73) Assignee: **Seiko Epson Corporation**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/078,447**

(22) Filed: **Nov. 12, 2013**

(65) **Prior Publication Data**

US 2014/0146111 A1 May 29, 2014

Related U.S. Application Data

(63) Continuation of application No. 13/046,671, filed on Mar. 11, 2011, now Pat. No. 8,616,682.

(30) **Foreign Application Priority Data**

Mar. 12, 2010 (JP) 2010-056806
May 28, 2010 (JP) 2010-122800

(51) **Int. Cl.**

B41J 2/045	(2006.01)
H01L 41/18	(2006.01)
B41J 2/055	(2006.01)
B41J 2/14	(2006.01)
B41J 2/16	(2006.01)
H01L 41/09	(2006.01)

(52) **U.S. Cl.**

CPC ***H01L 41/183*** (2013.01); ***B41J 2/045*** (2013.01); ***B41J 2/055*** (2013.01); ***B41J 2/14233*** (2013.01); ***B41J 2/161*** (2013.01); ***B41J 2/1623*** (2013.01); ***B41J 2/1629*** (2013.01); ***B41J 2/1634*** (2013.01); ***B41J 2/1645*** (2013.01); ***B41J 2/1646*** (2013.01); ***H01L 41/0973*** (2013.01); ***H01L 41/18*** (2013.01); *B41J 2002/14241* (2013.01); *B41J 2002/14419* (2013.01); *B41J 2202/03* (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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Primary Examiner — Erica Lin

(74) *Attorney, Agent, or Firm* — Kilpatrick Townsend & Stockton LLP

(57) **ABSTRACT**

A liquid ejection head, comprises a pressure generation chamber communicating with a nozzle opening and a piezoelectric element having a piezoelectric layer and an electrodes. The piezoelectric layer is a perovskite type complex oxide containing bismuth, iron, and cerium. The piezoelectric layer contains the cerium in a proportion of 0.01 molar ratio or more and 0.13 molar ratio or lower based on the total amount of the bismuth and the cerium.

9 Claims, 18 Drawing Sheets

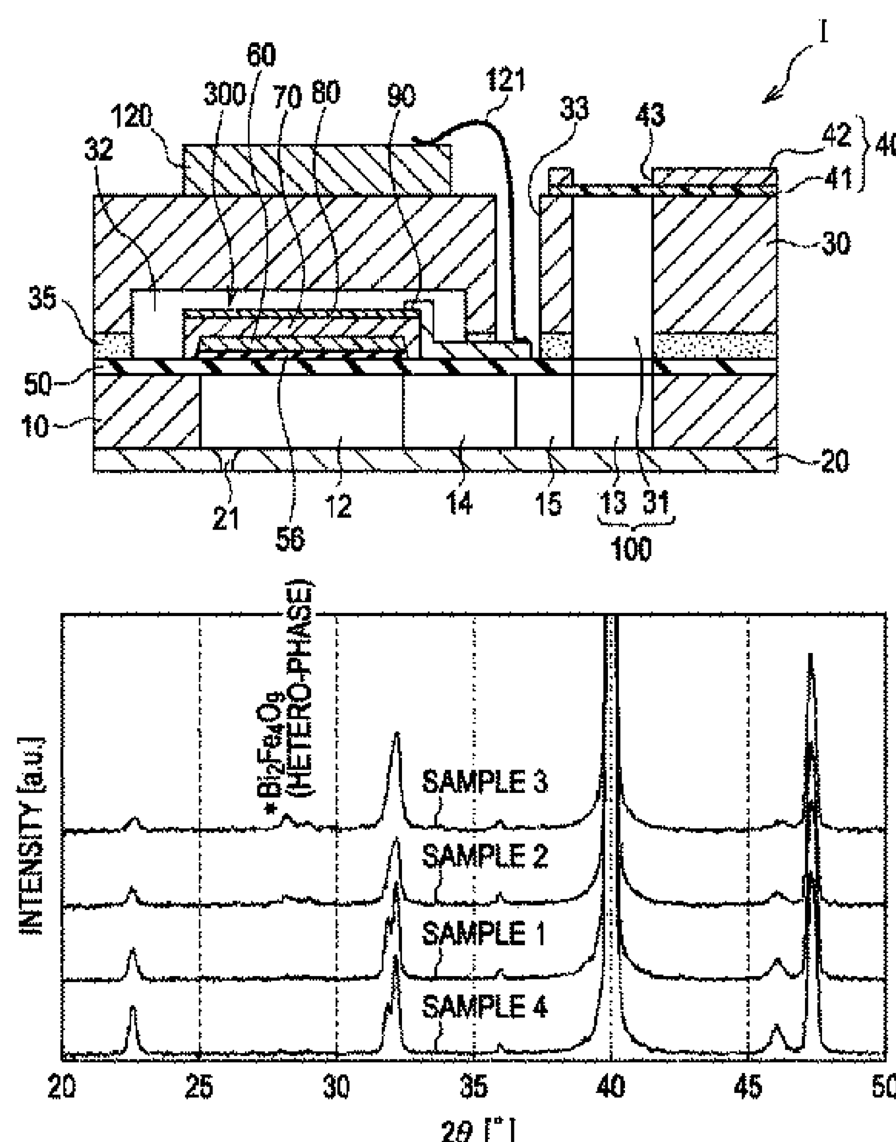

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FIG. 1

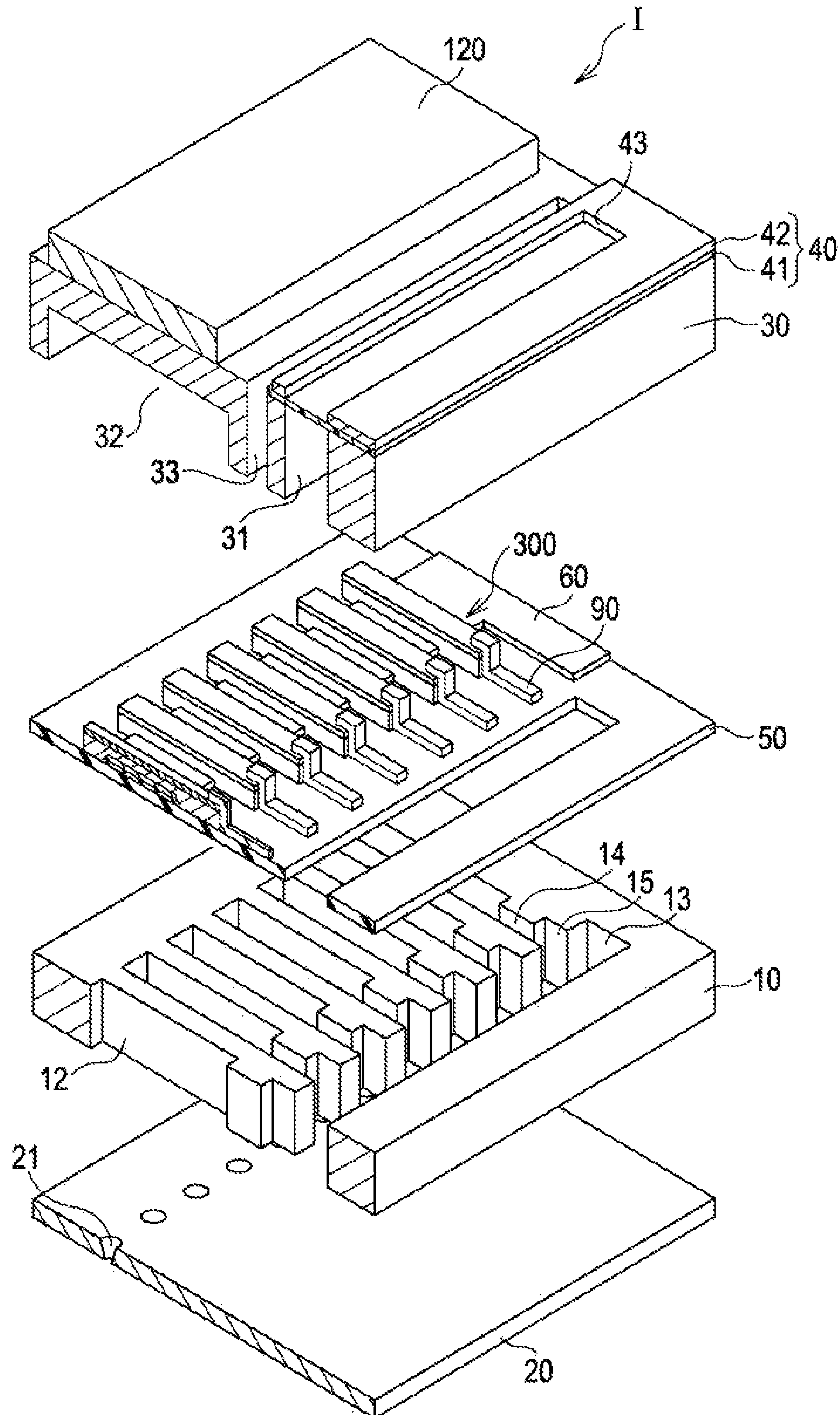


FIG. 2

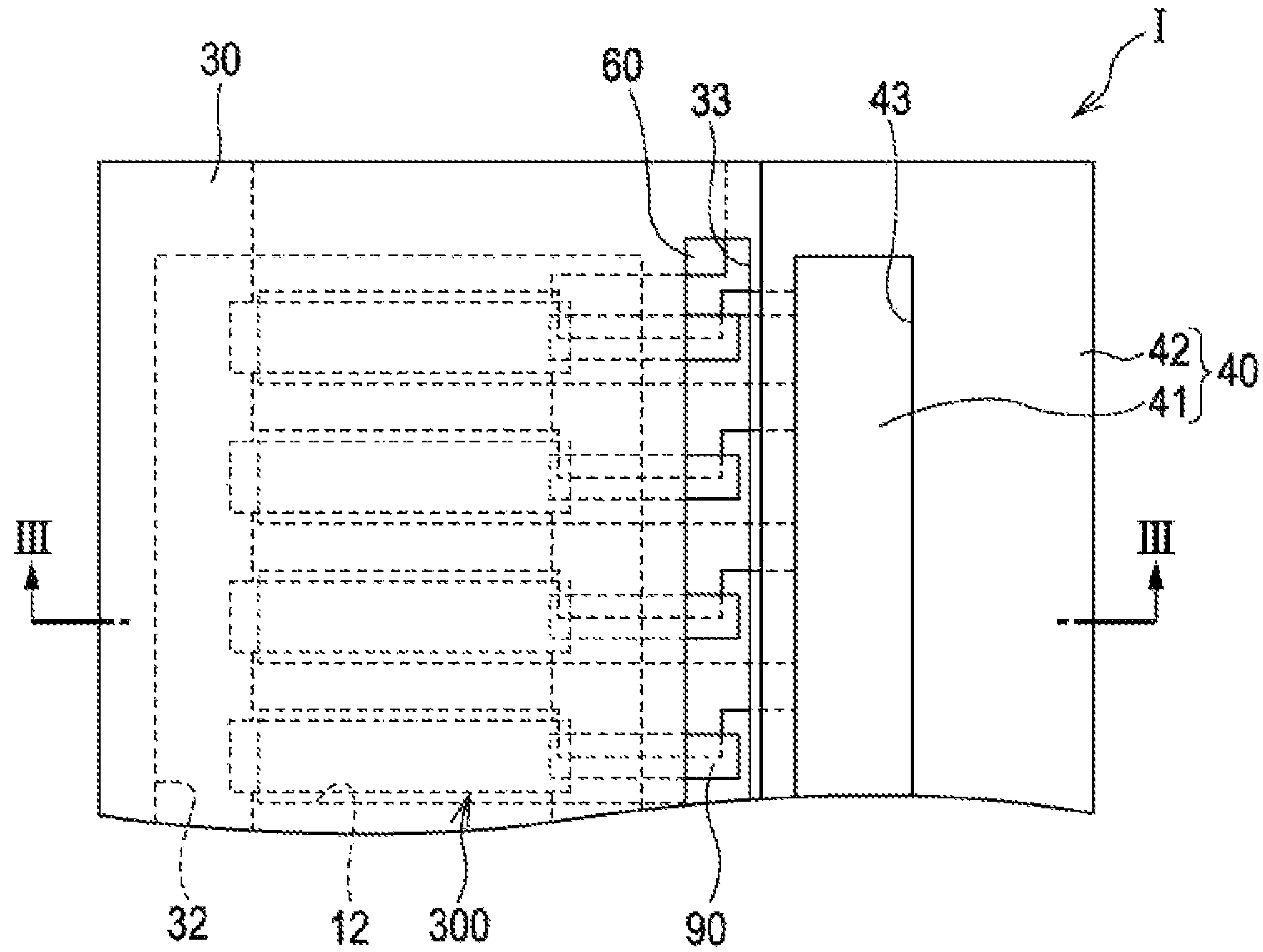


FIG. 3

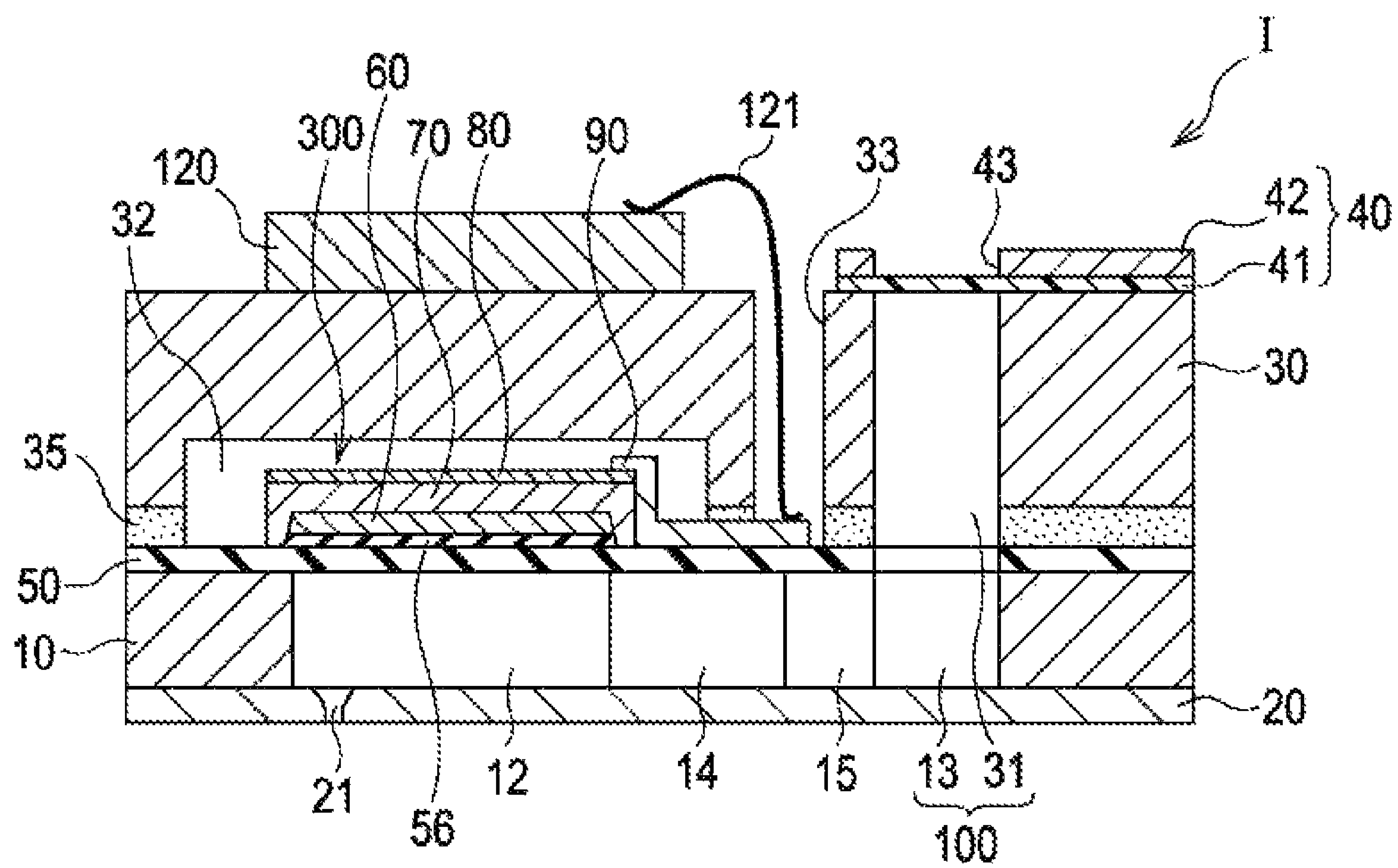


FIG. 4

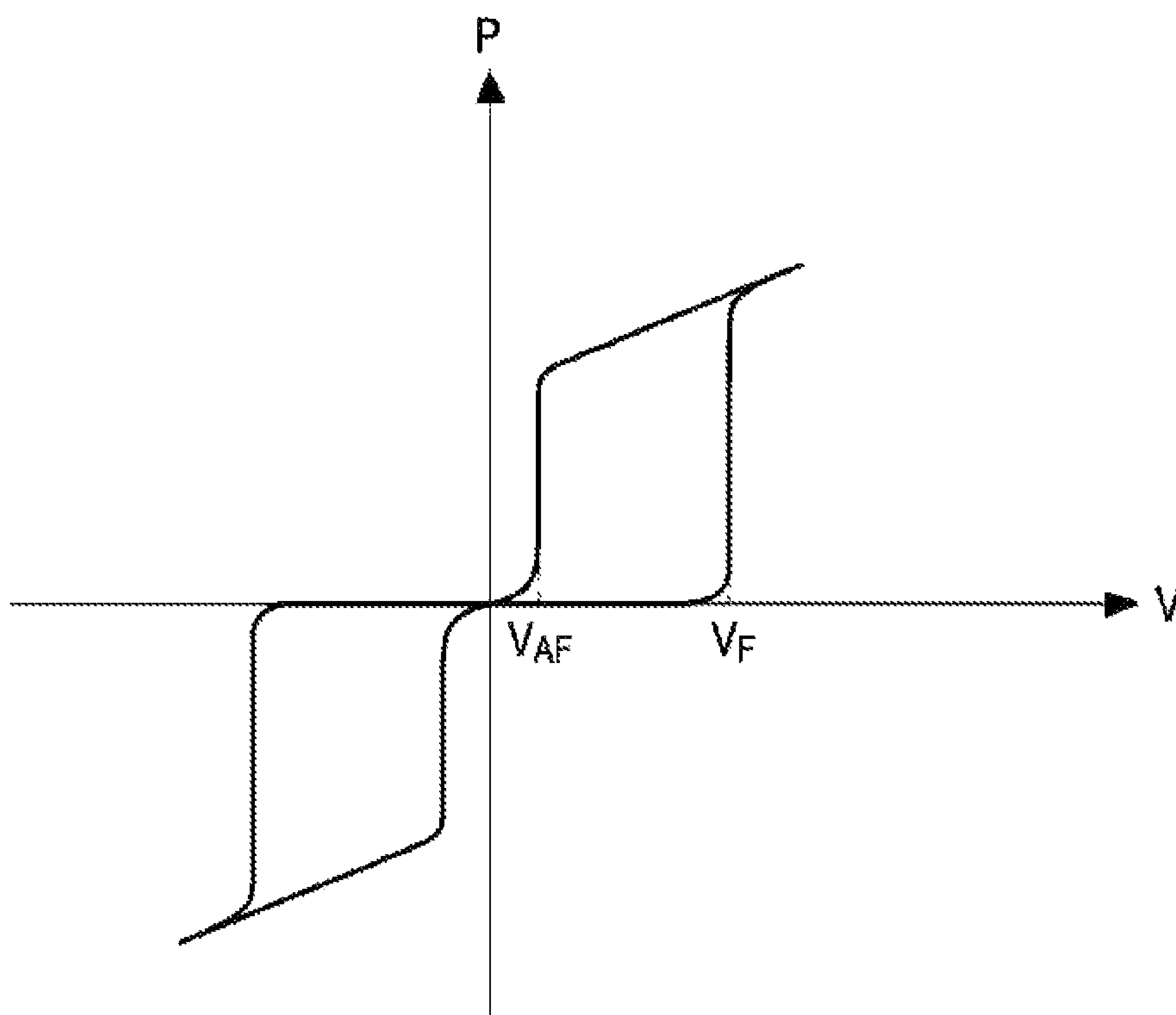


FIG. 5A

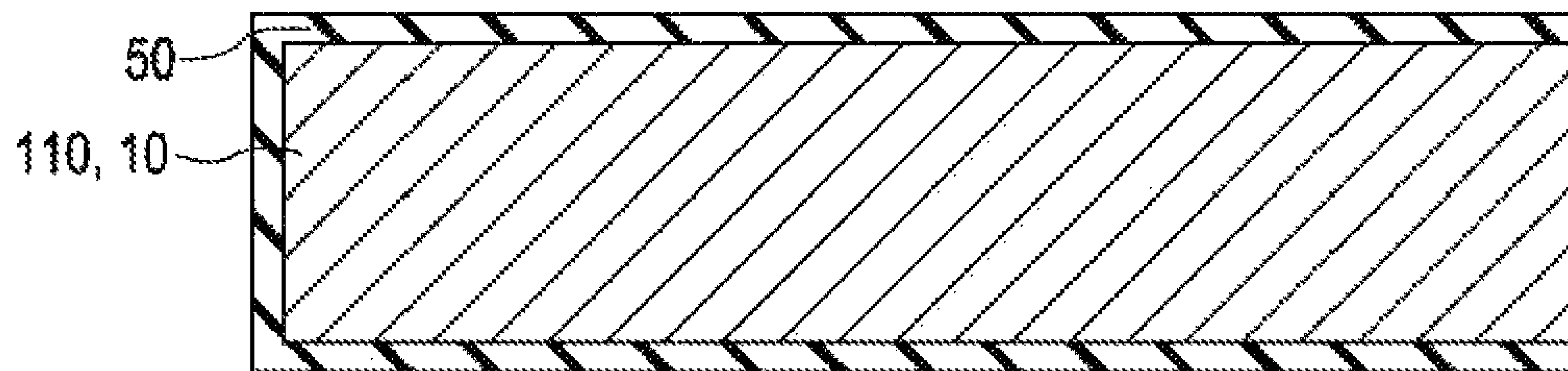


FIG. 5B

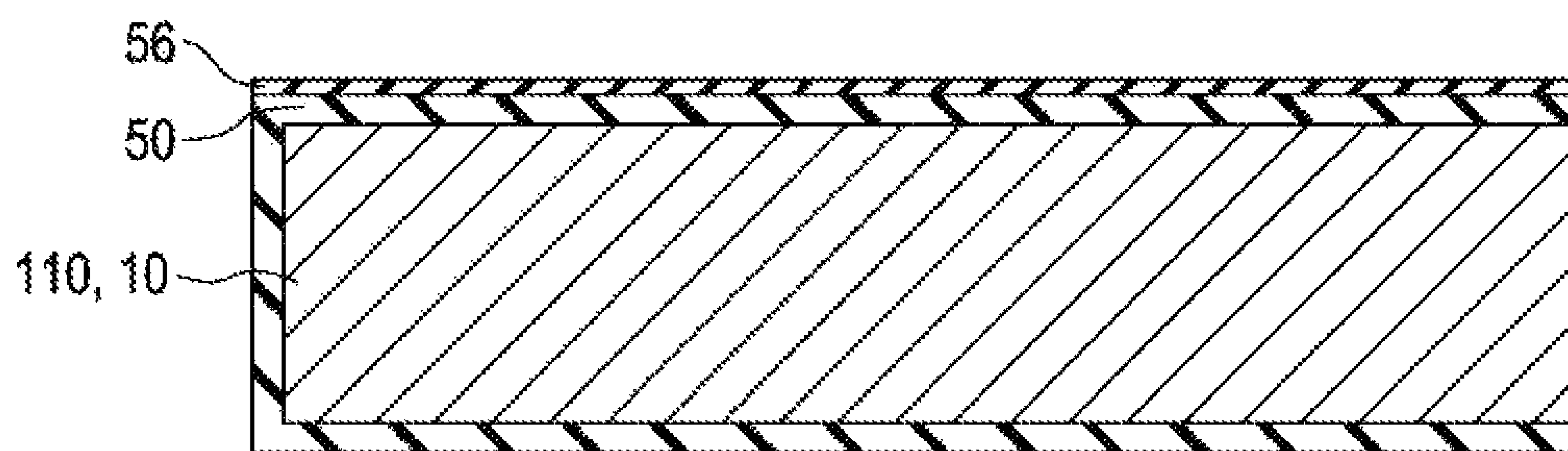


FIG. 6A

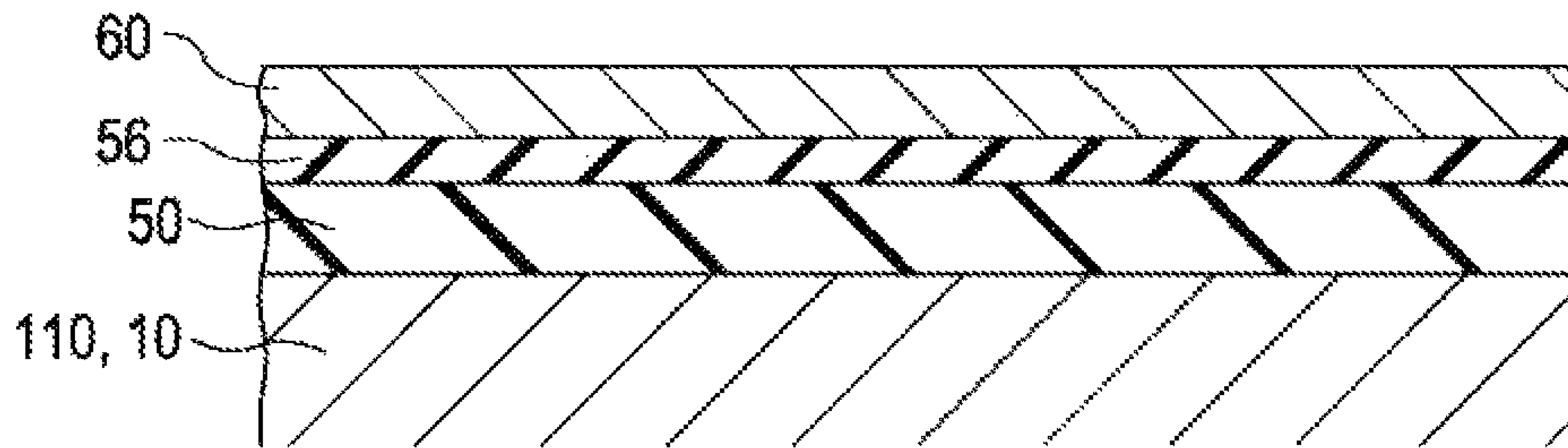


FIG. 6B

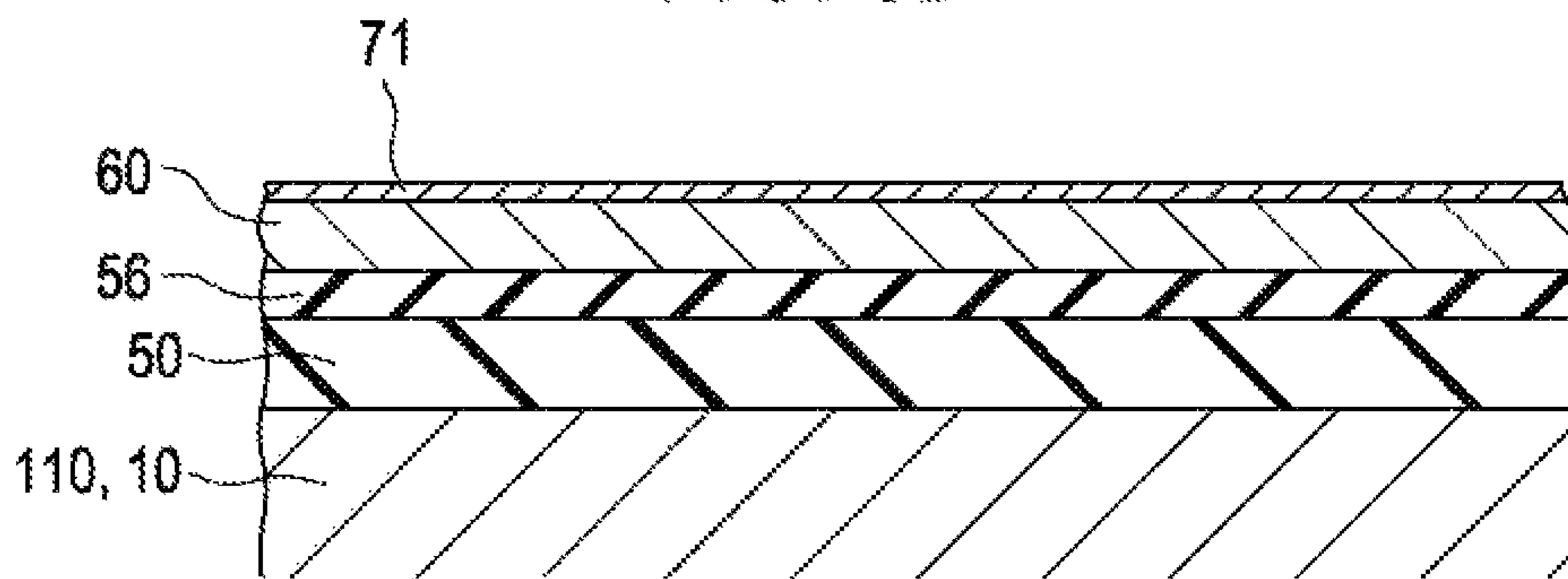


FIG. 6C

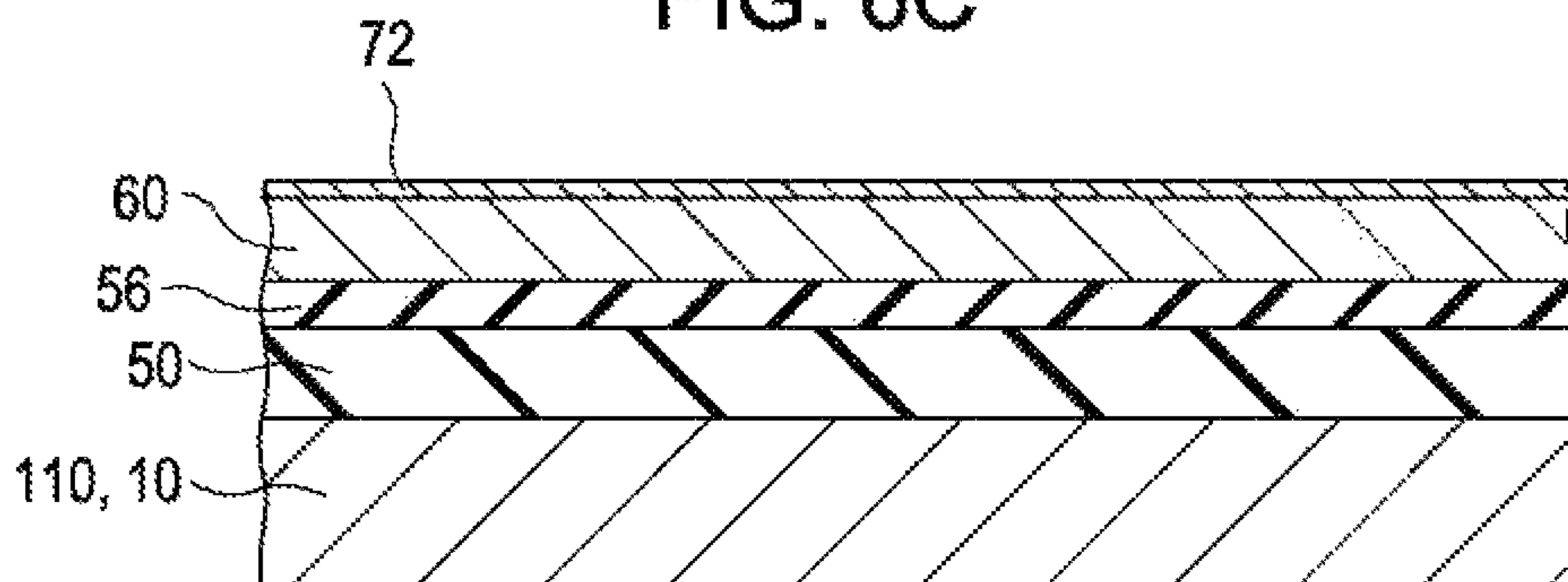


FIG. 7A

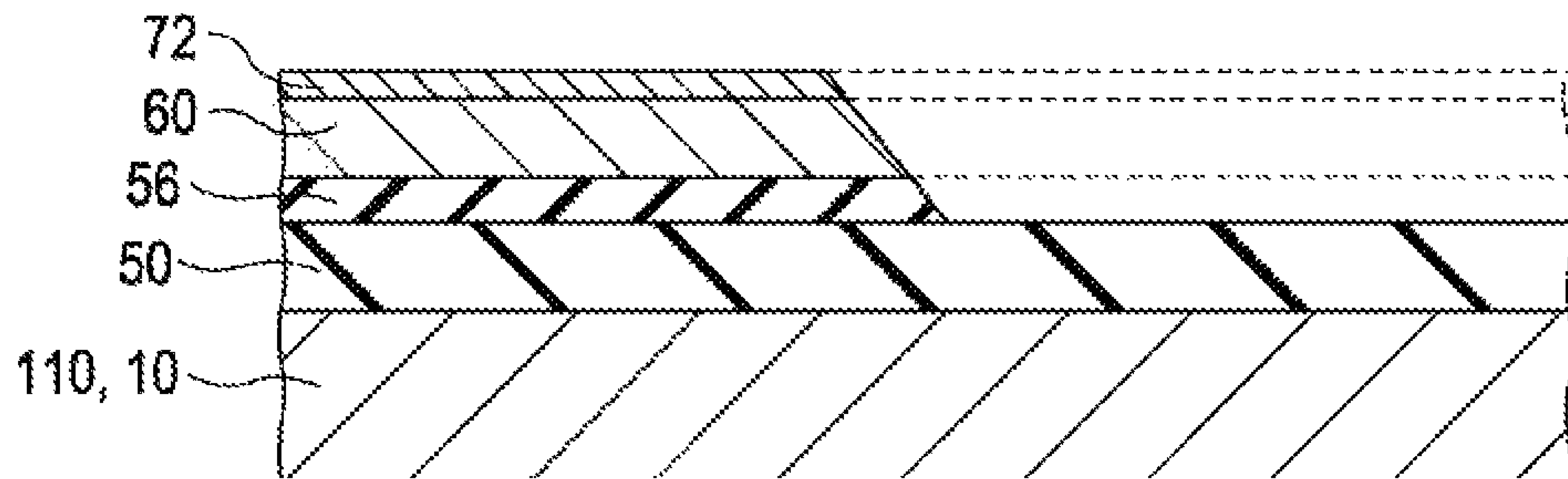


FIG. 7B

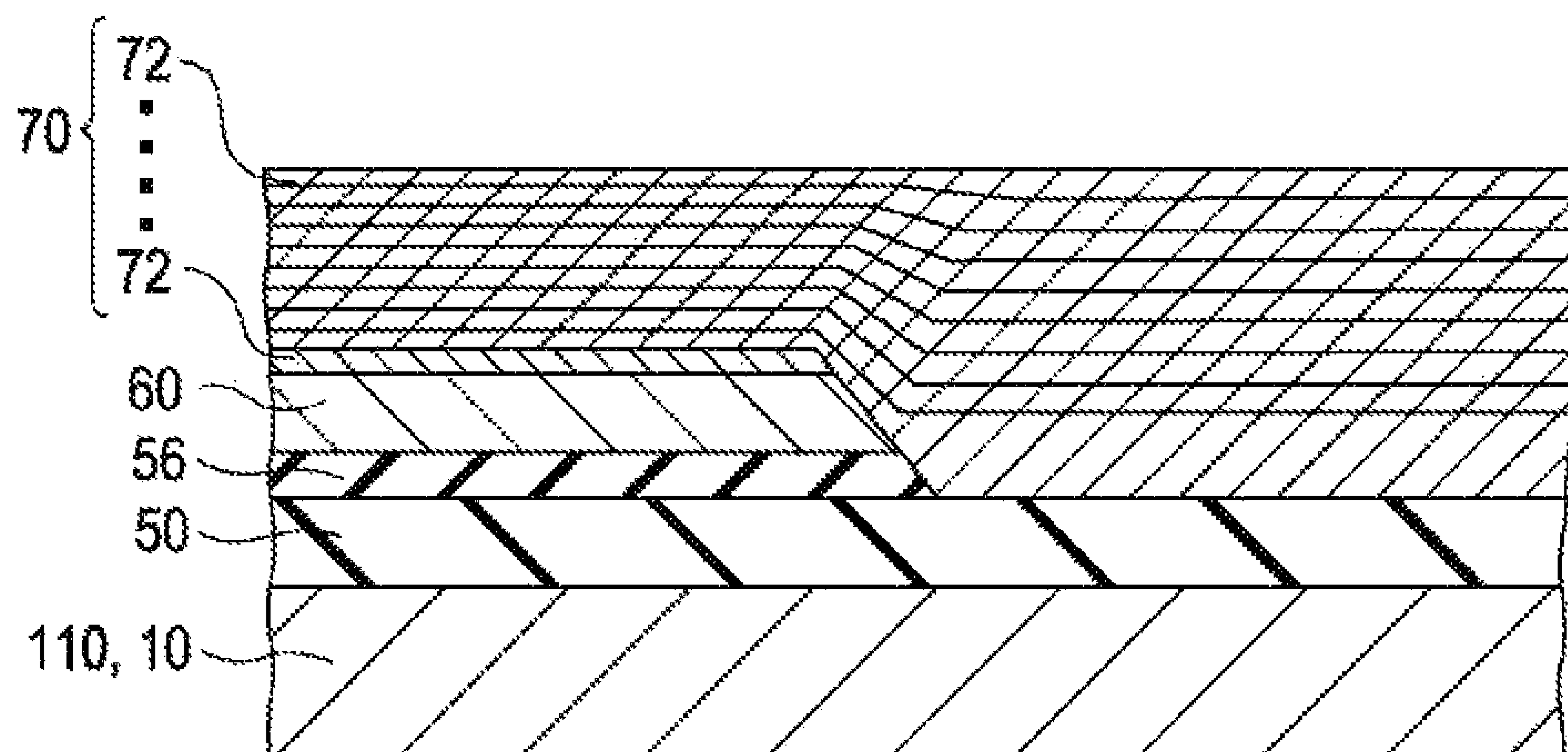


FIG. 8A

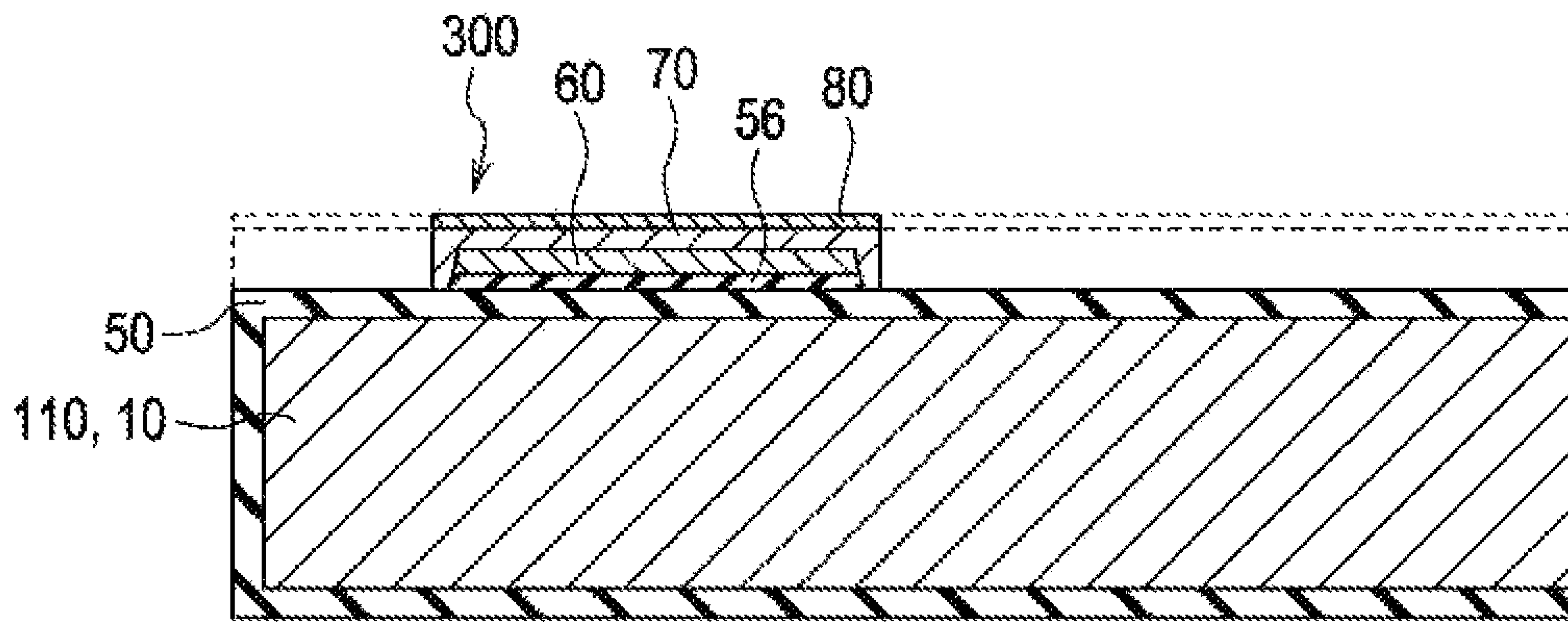


FIG. 8B

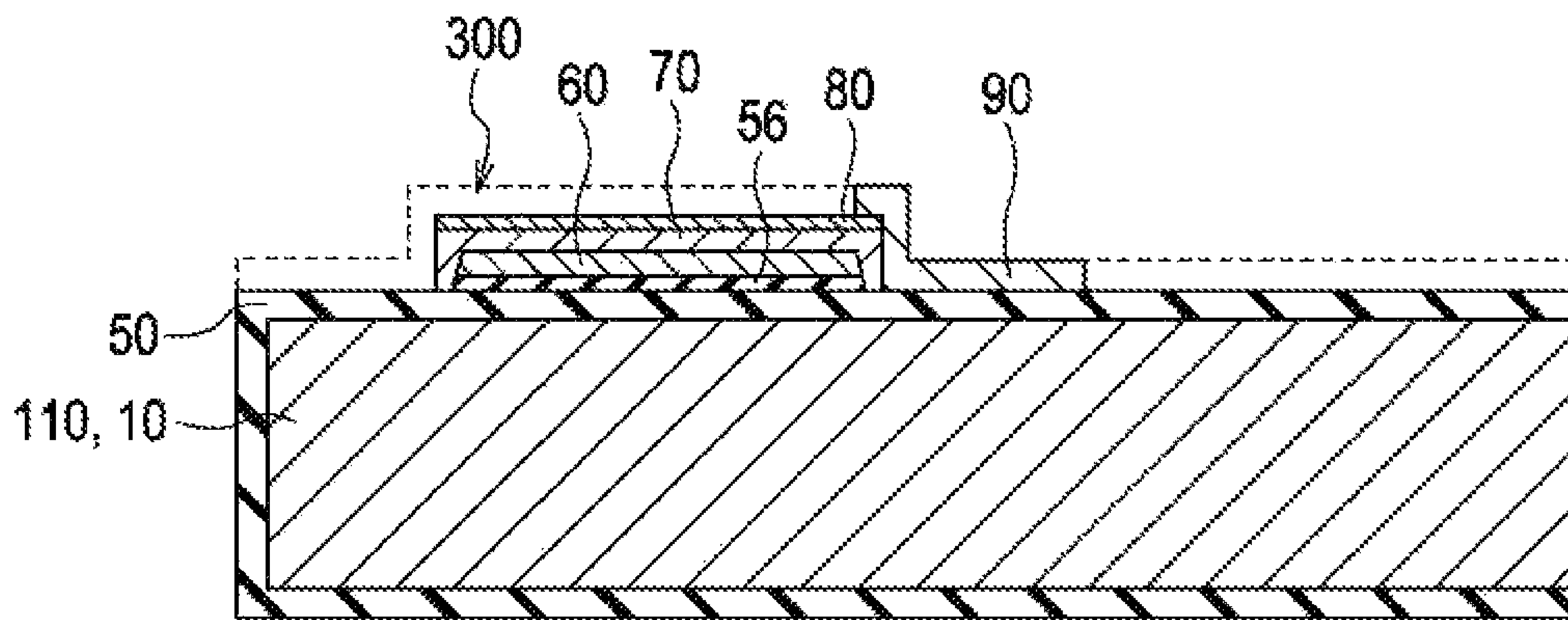


FIG. 8C

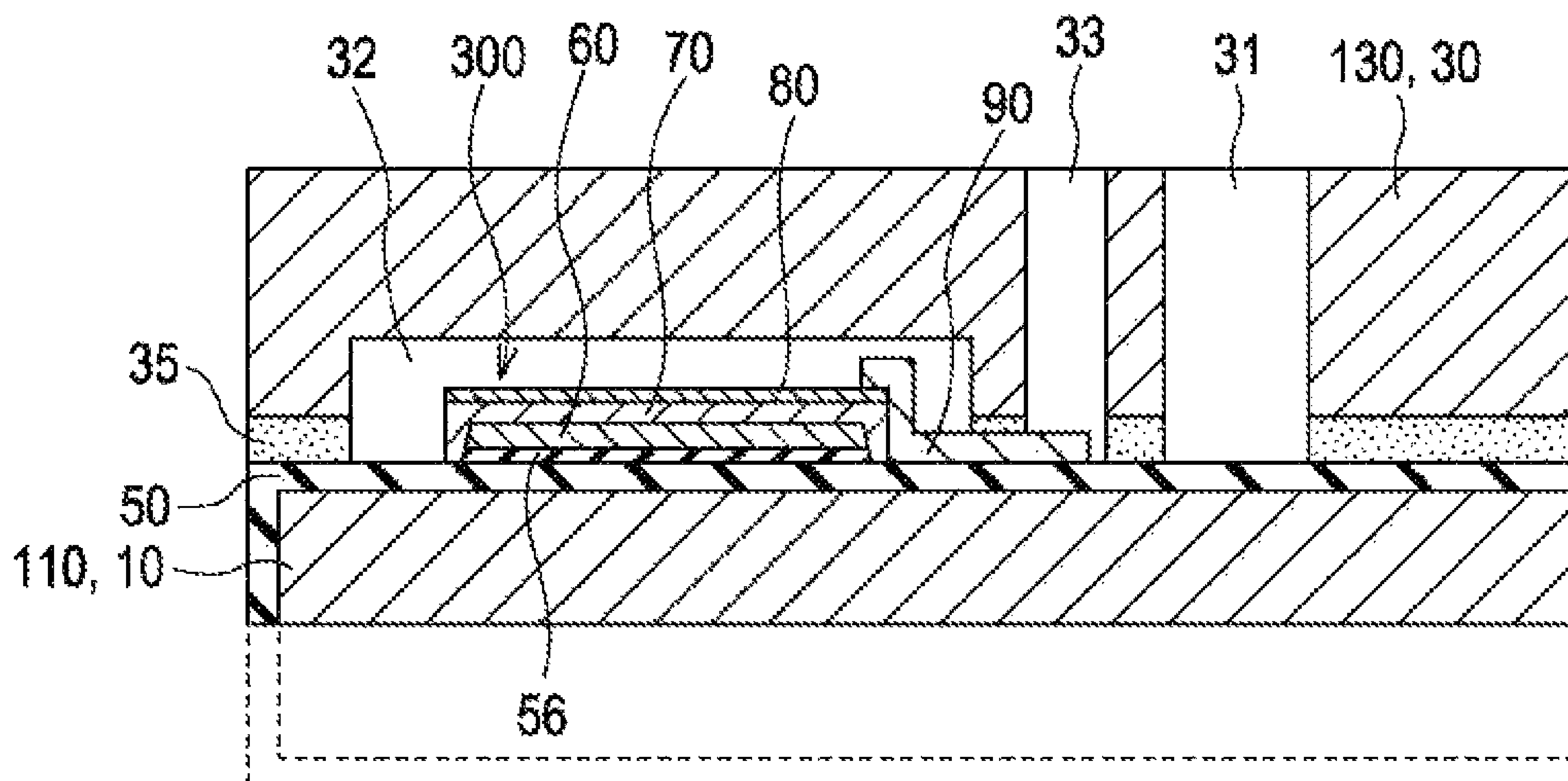


FIG. 9A

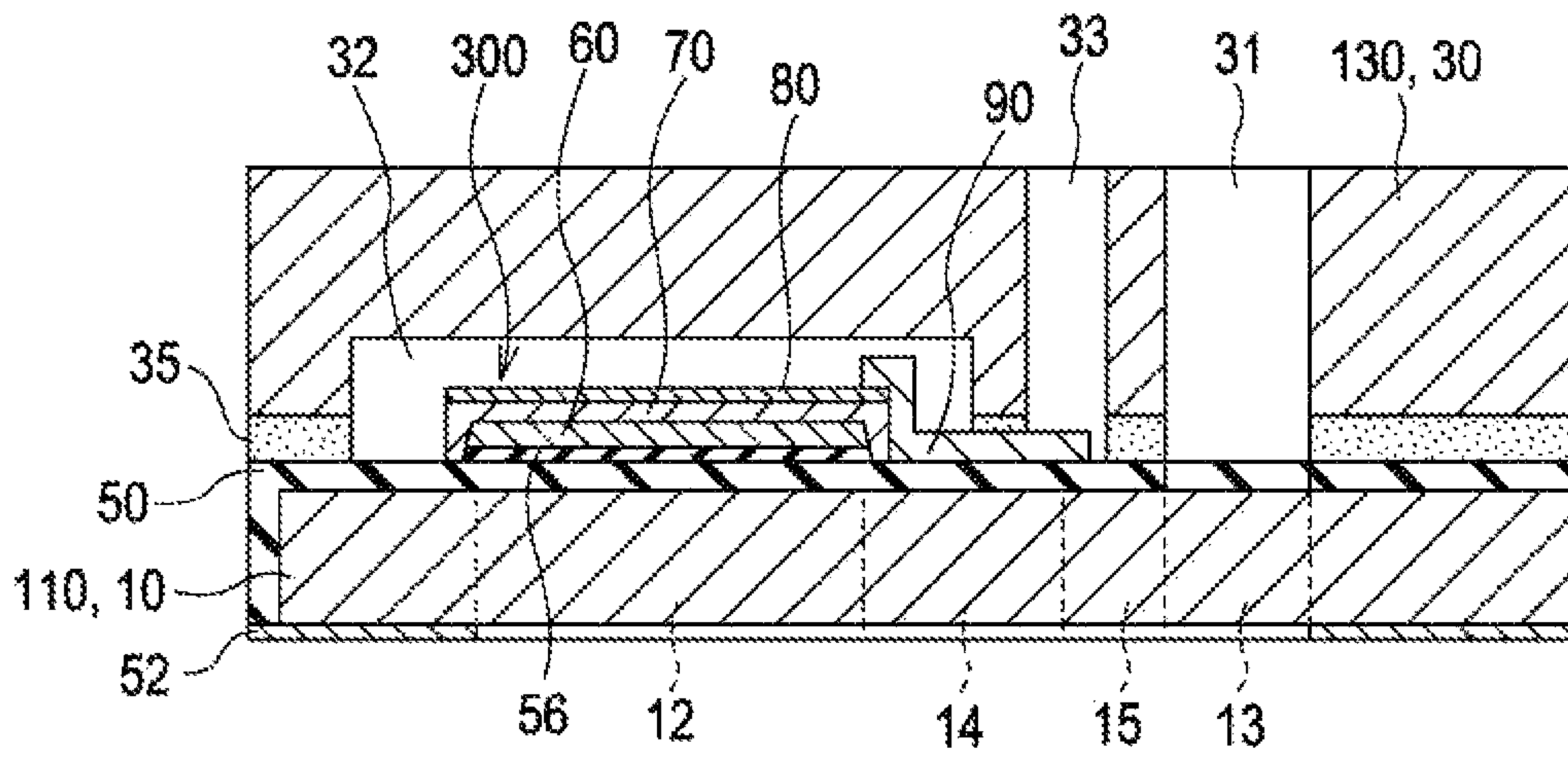
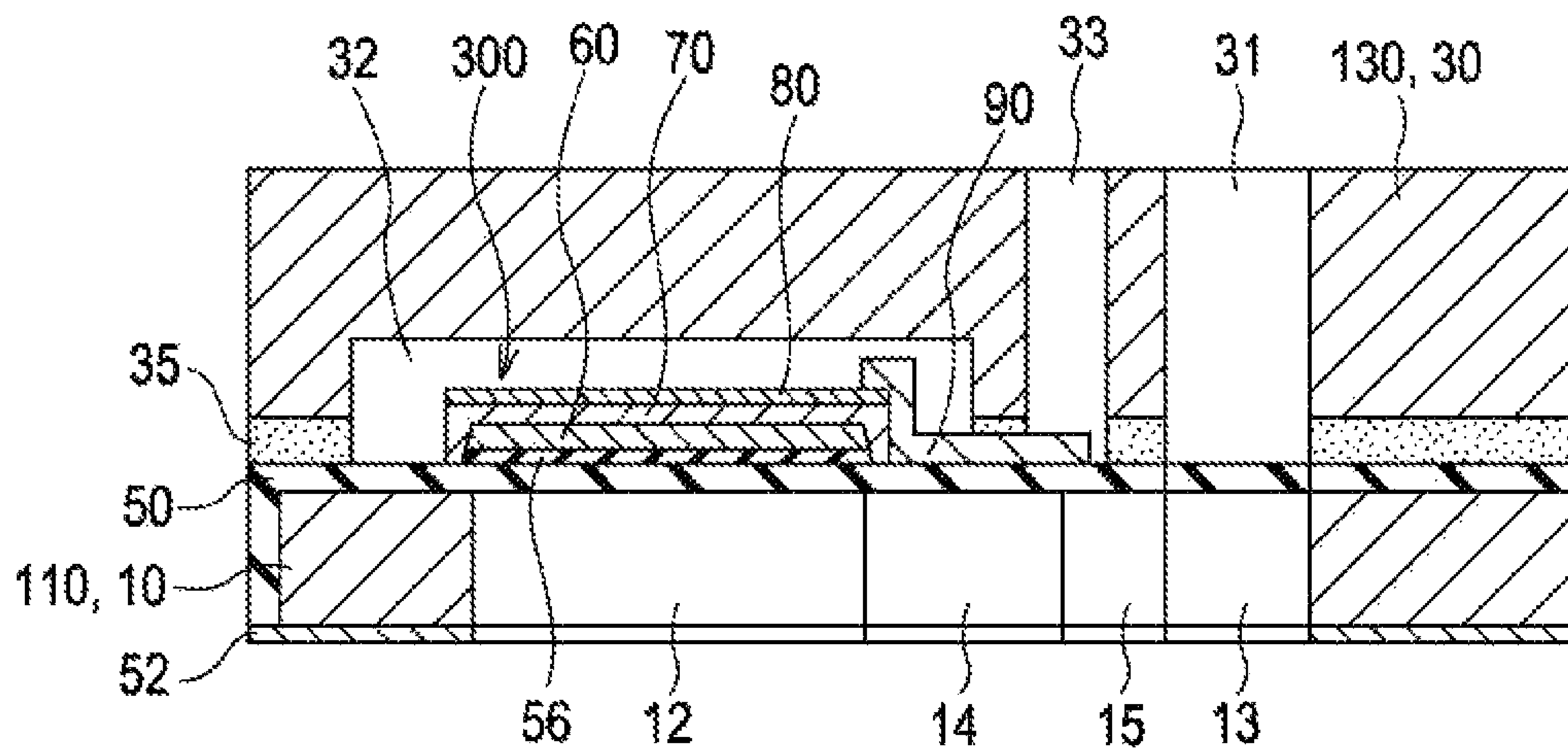


FIG. 9B



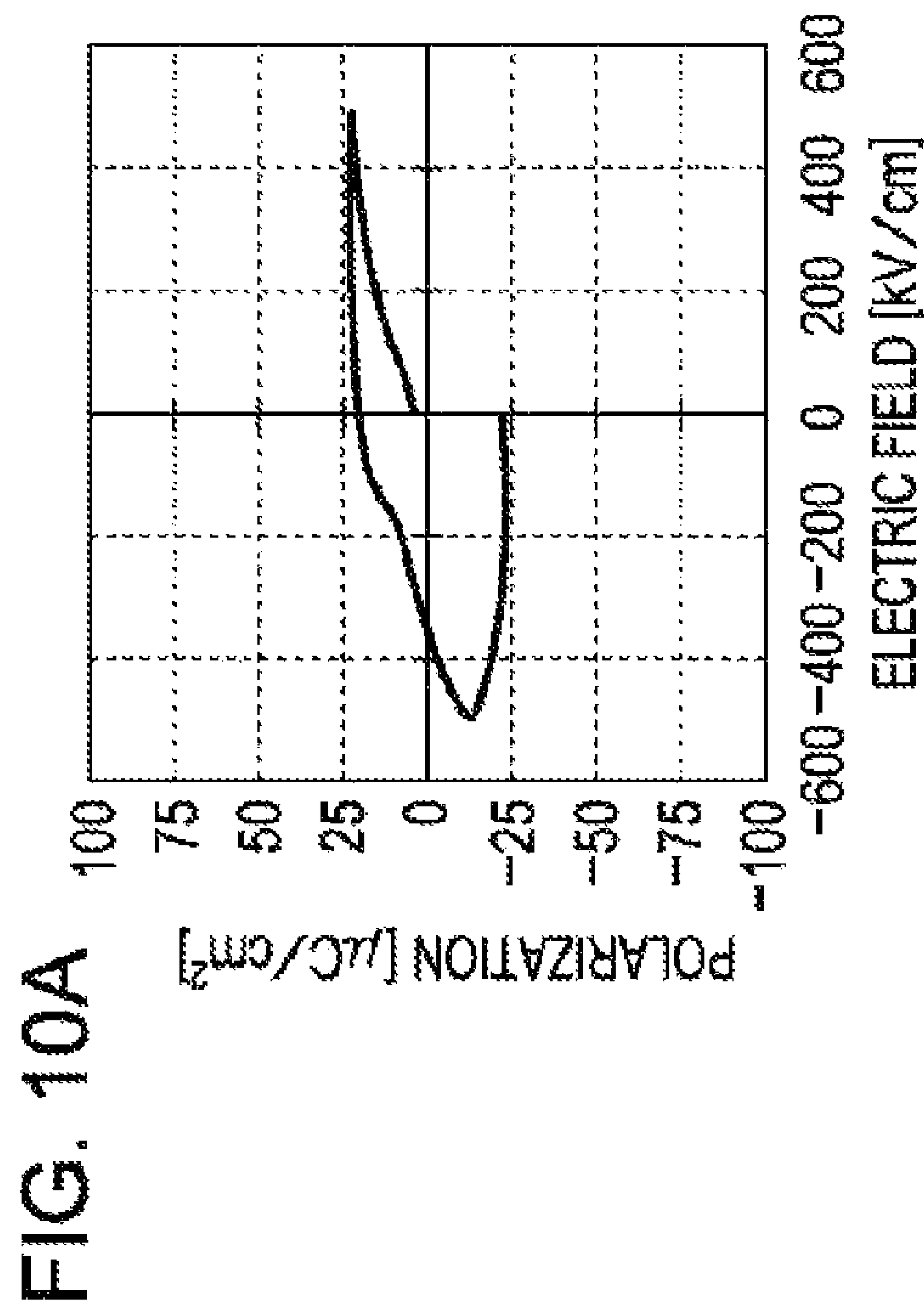


FIG. 10A

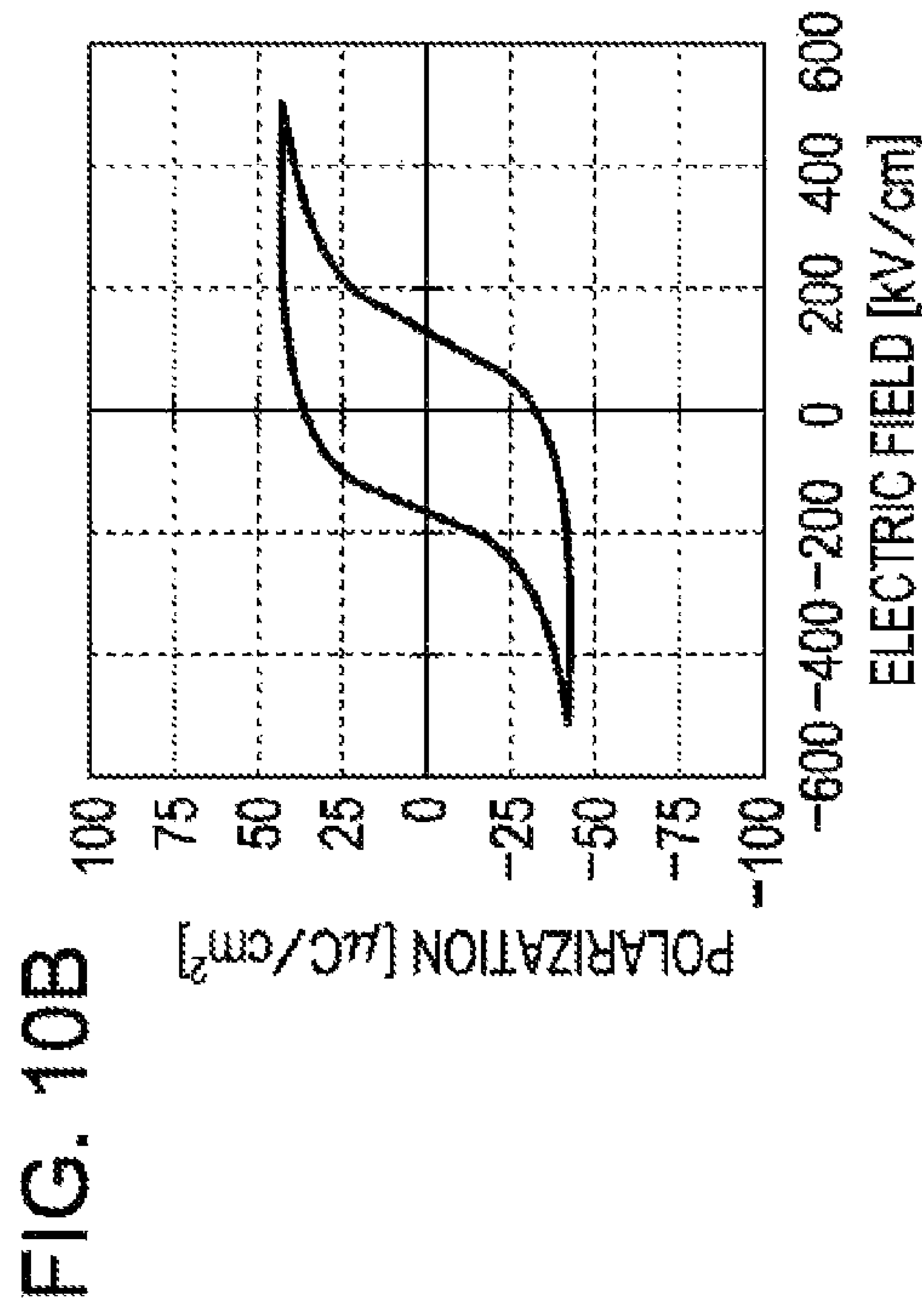


FIG. 10B

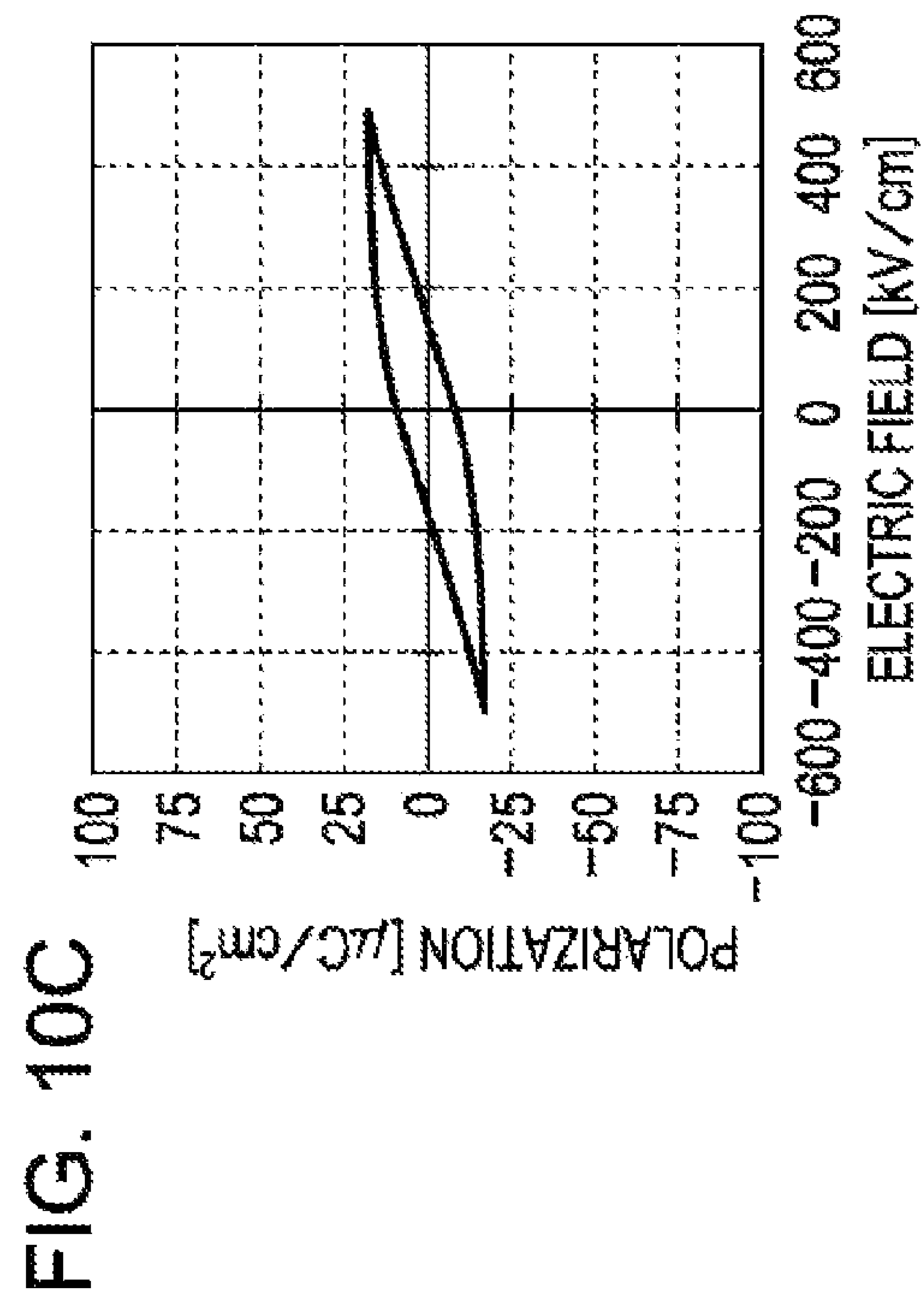


FIG. 10C

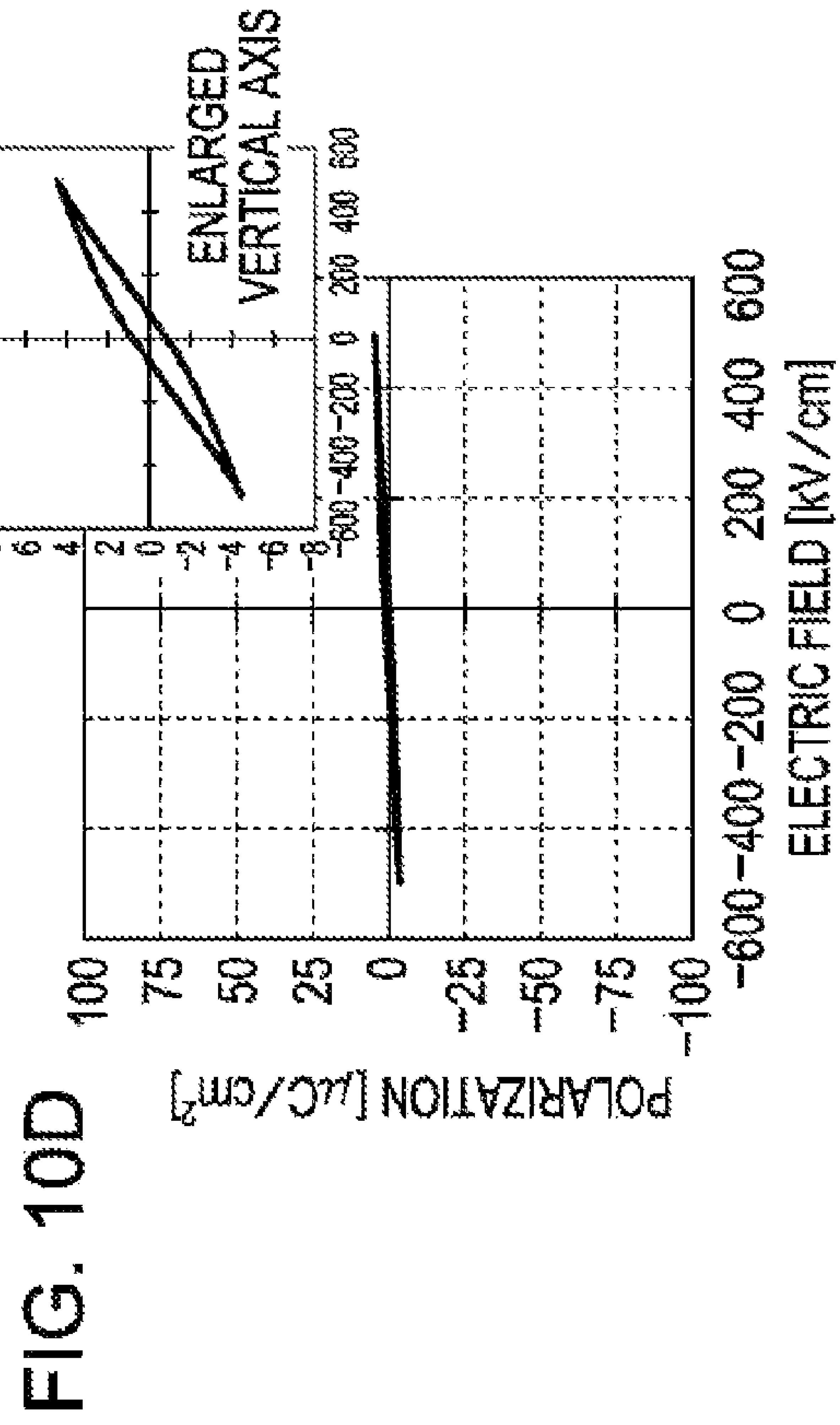


FIG. 10D

FIG. 11

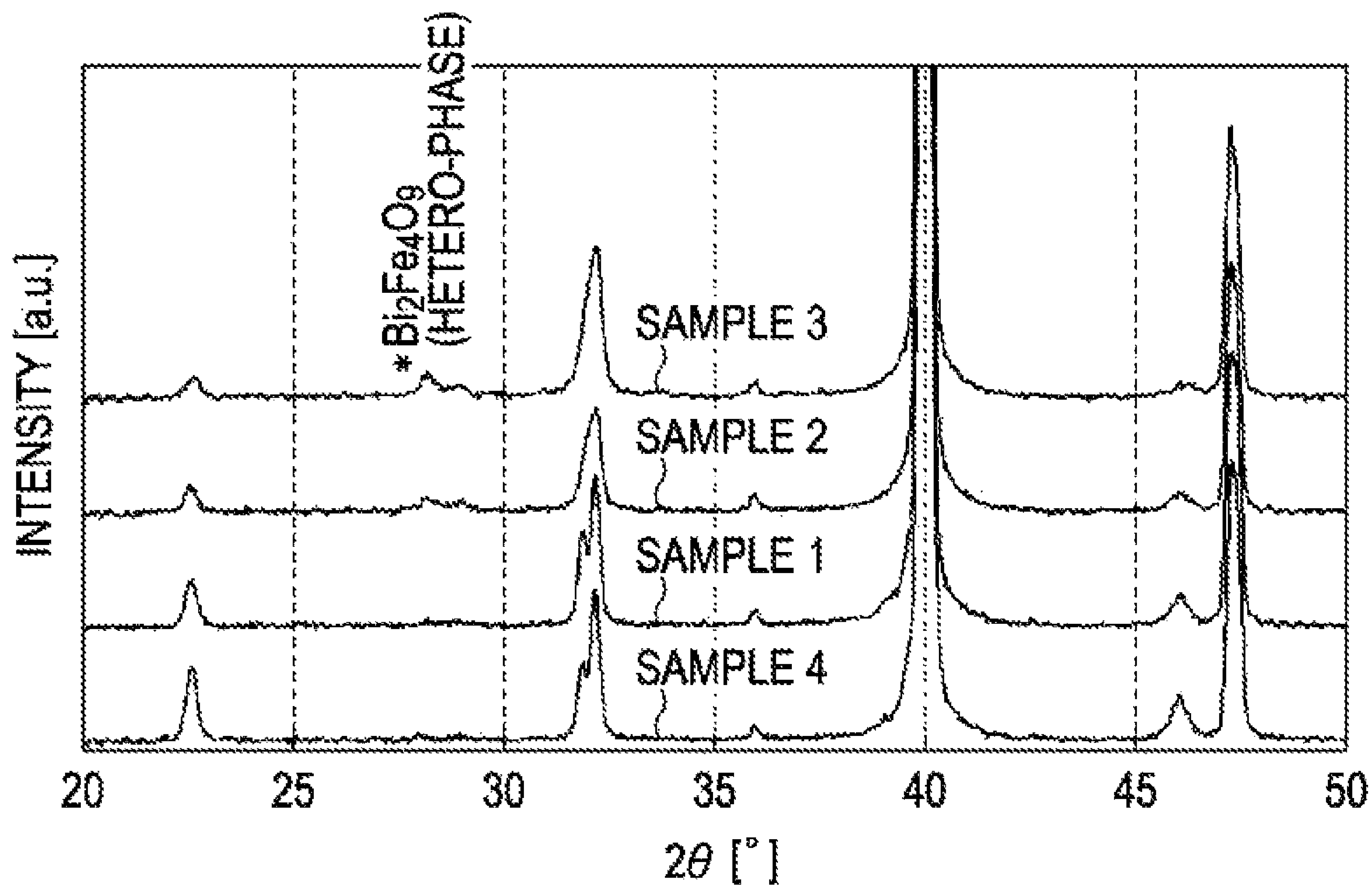


FIG. 12

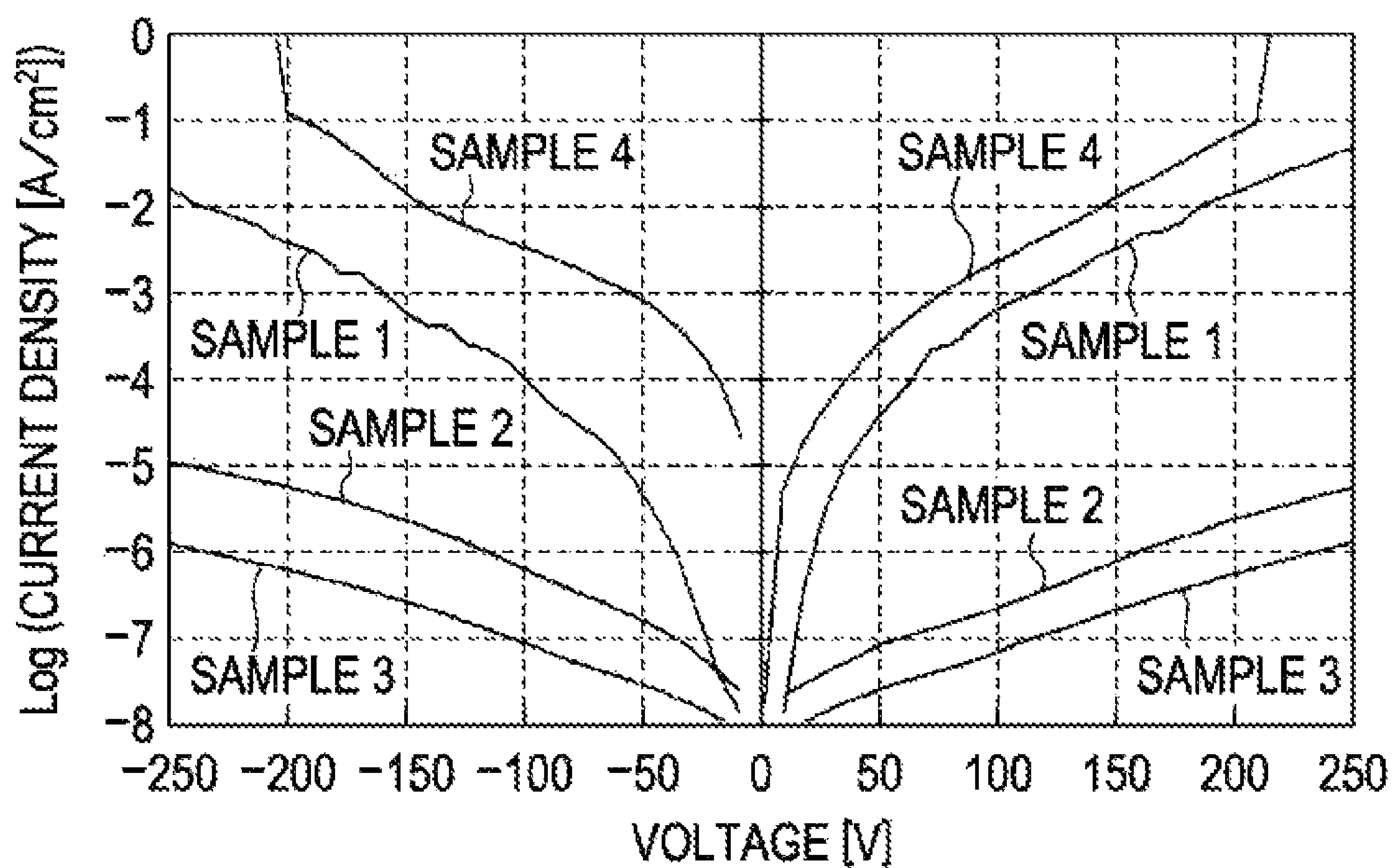


FIG. 13

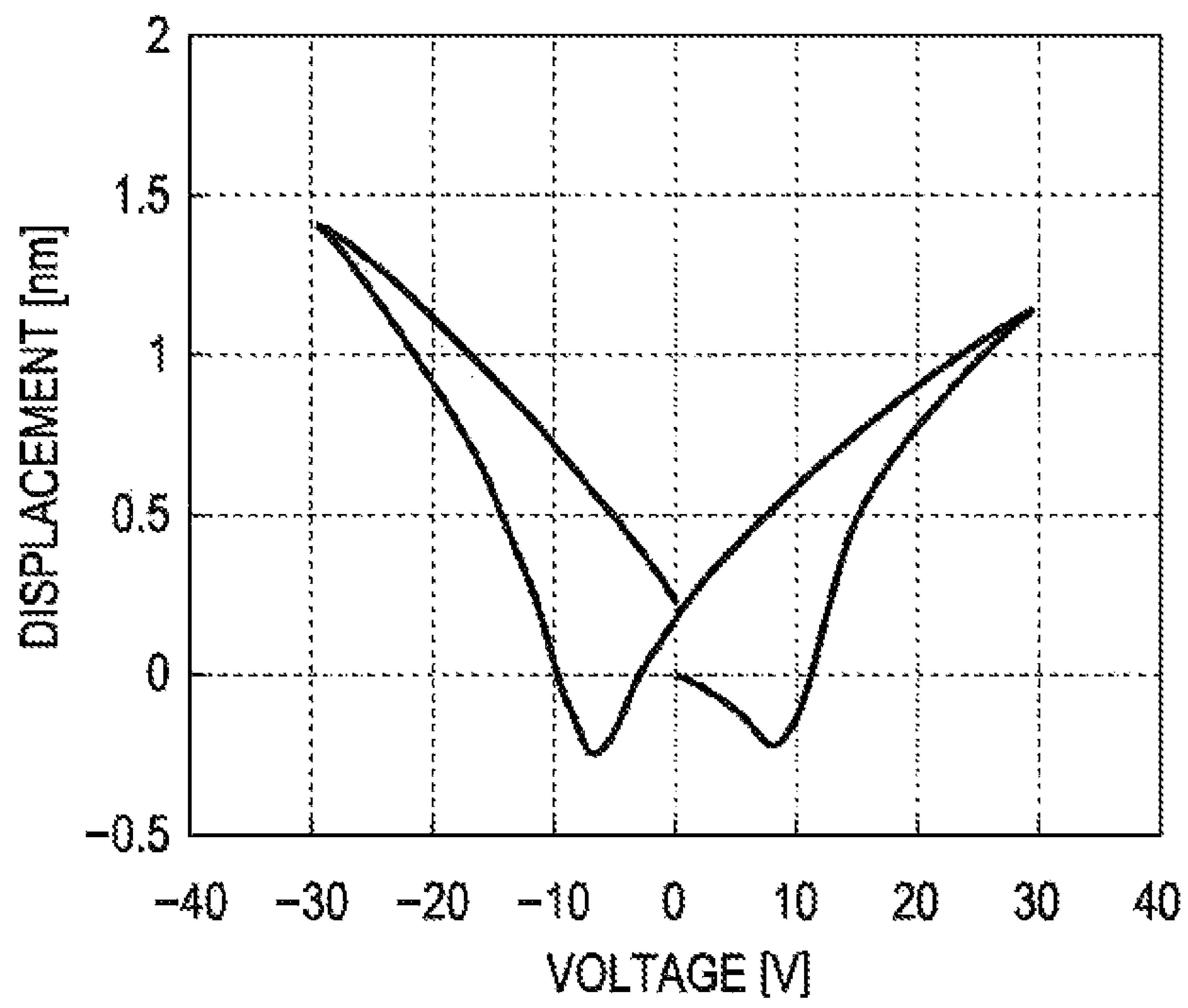


FIG. 14A

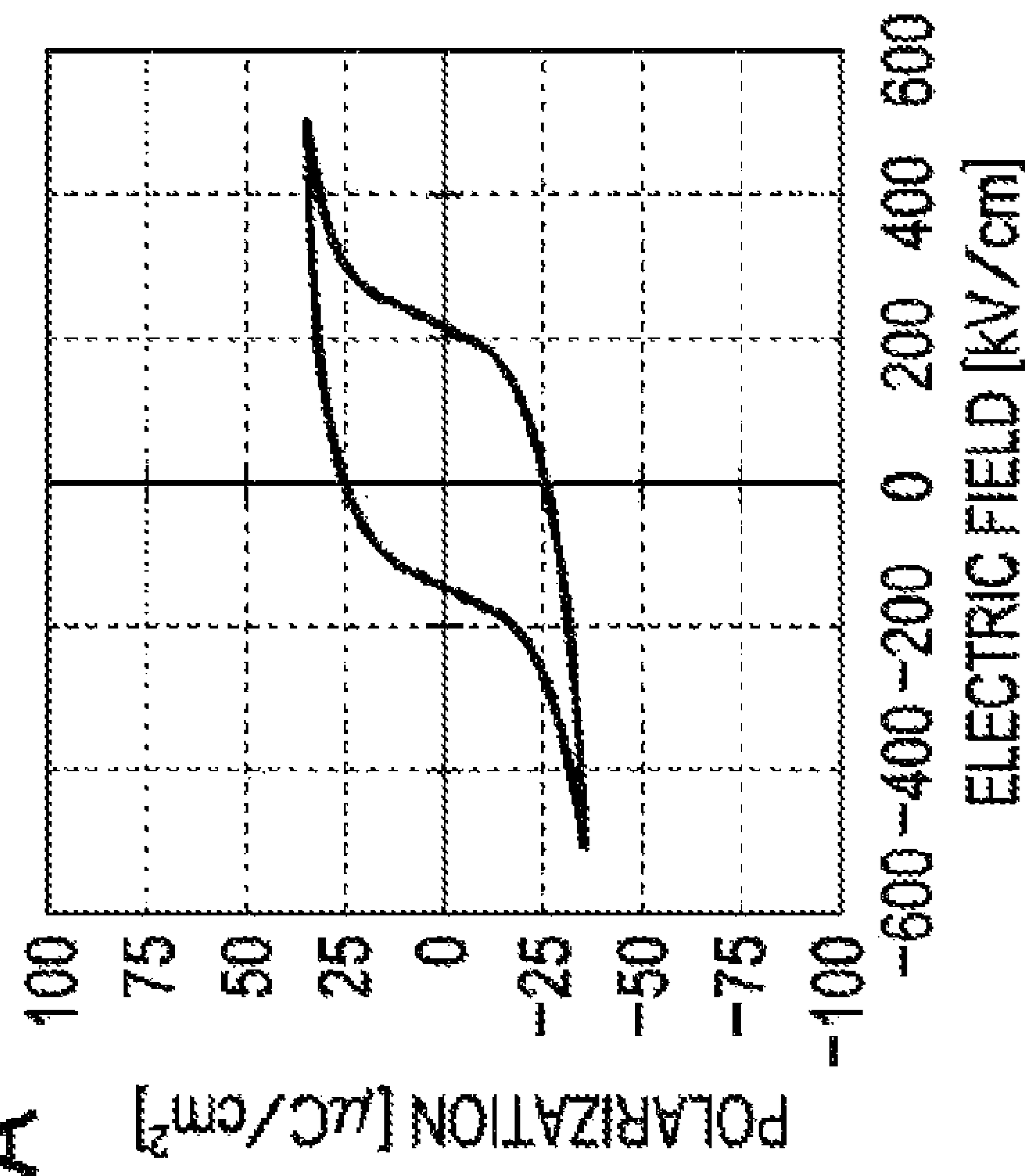


FIG. 14B

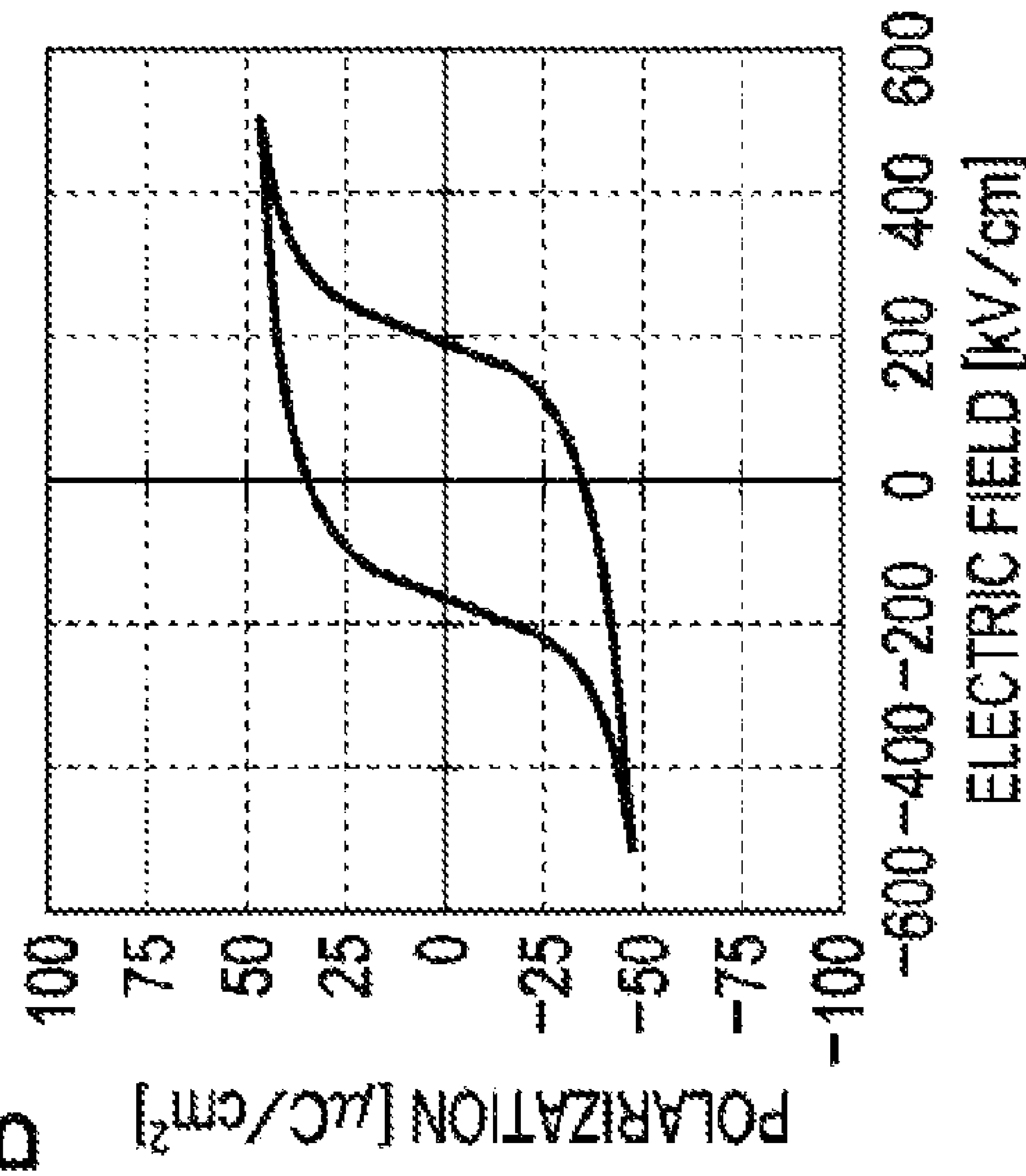


FIG. 14C

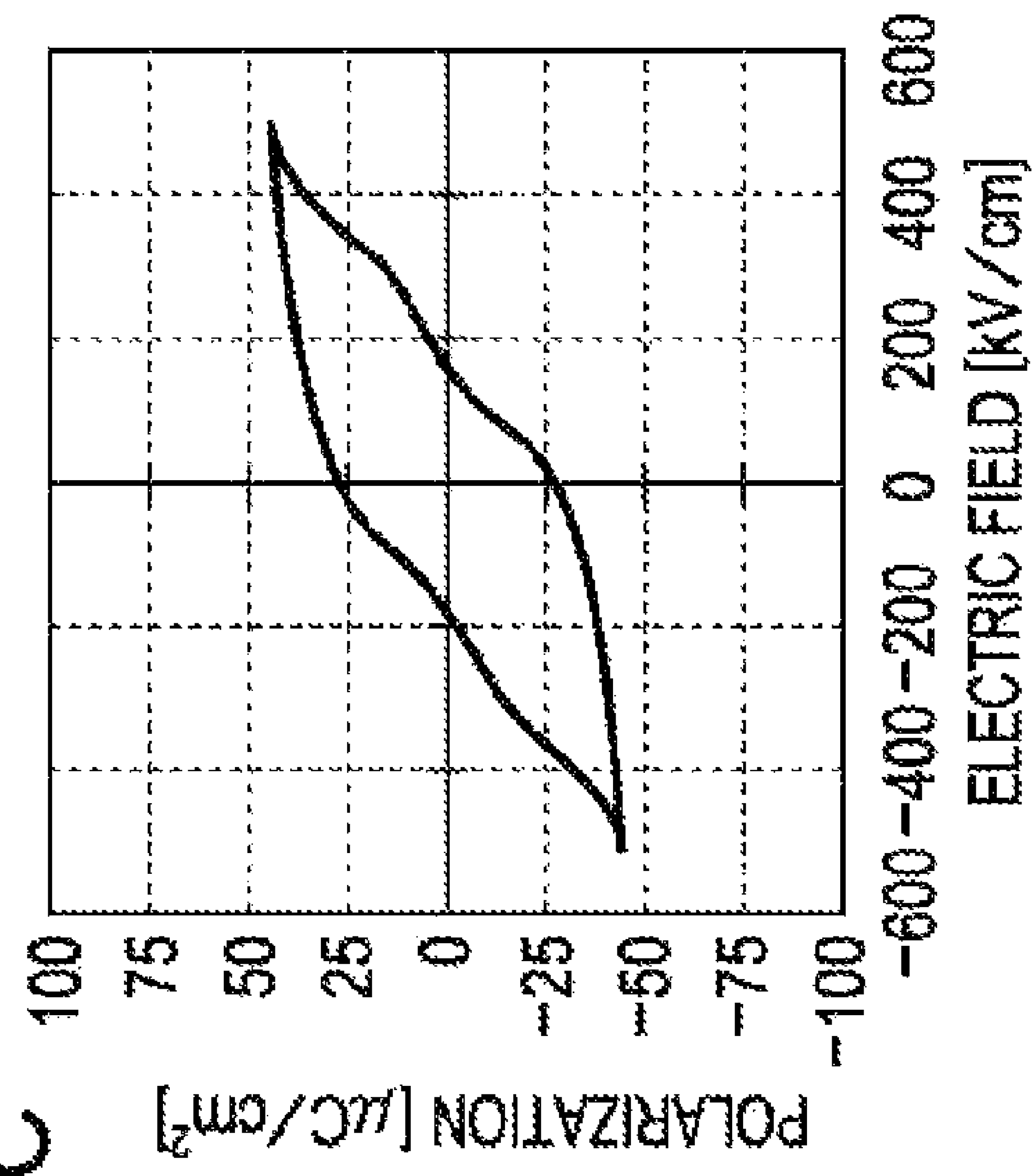


FIG. 14D

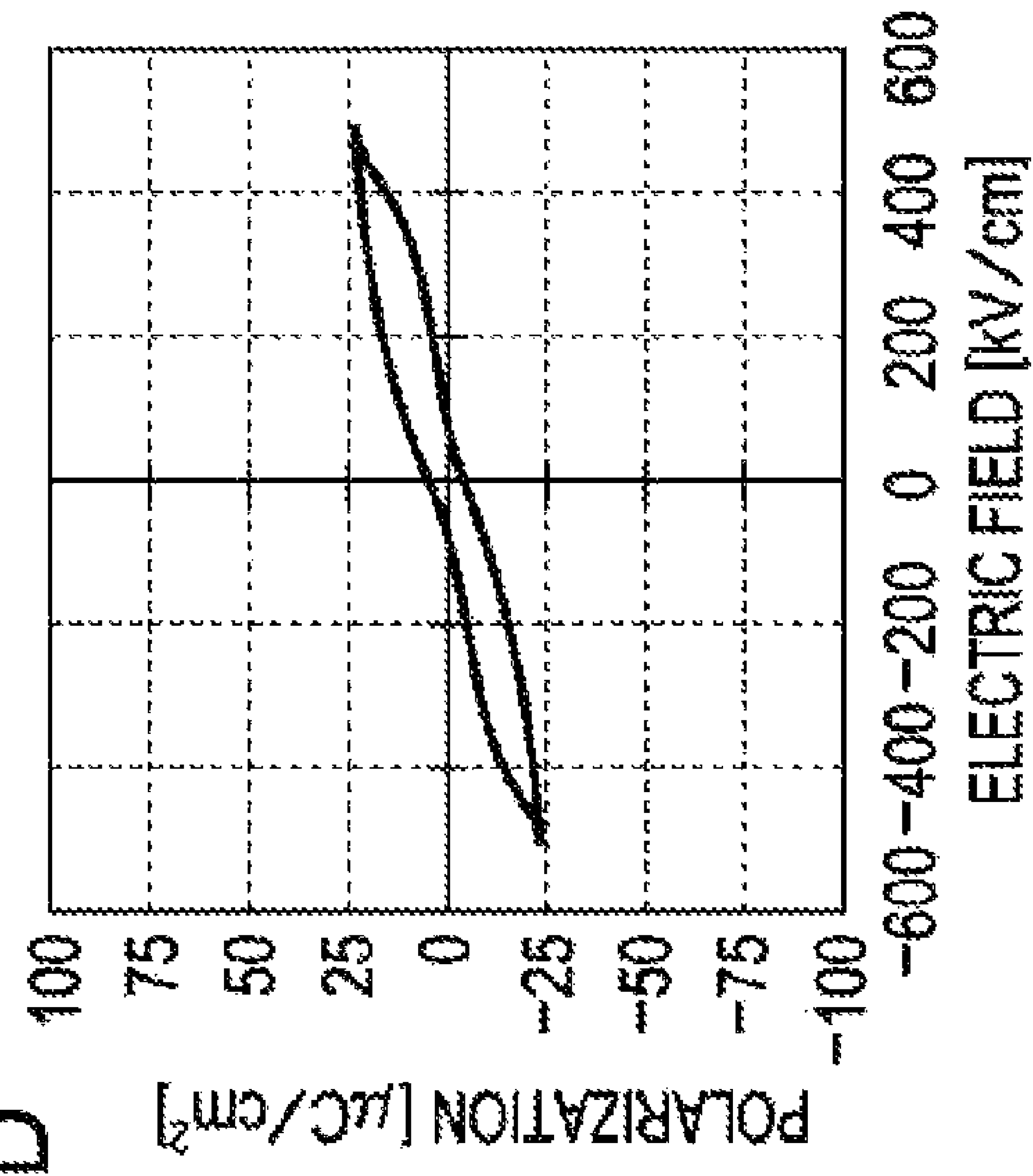


FIG. 15

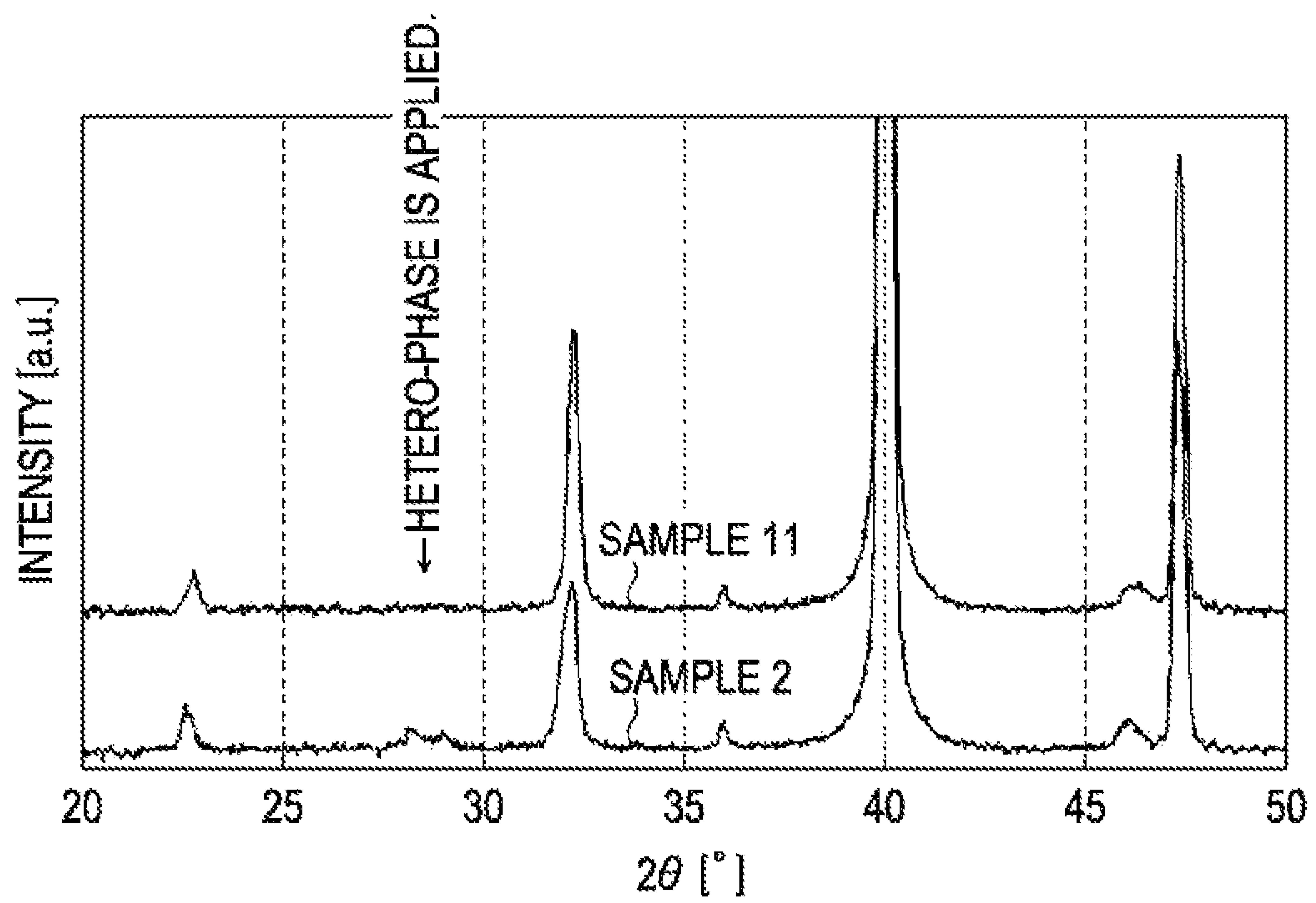


FIG. 16B

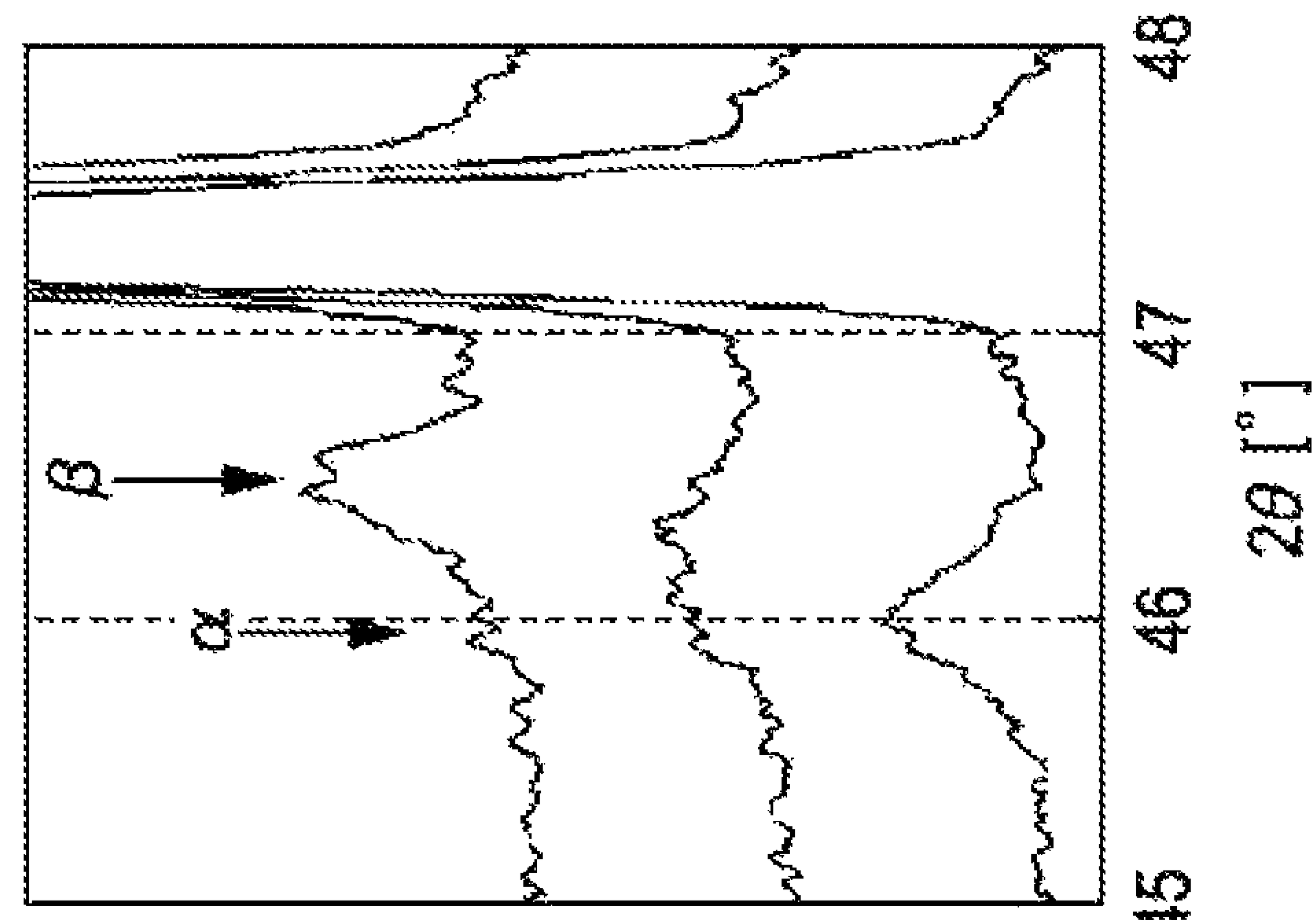


FIG. 16A

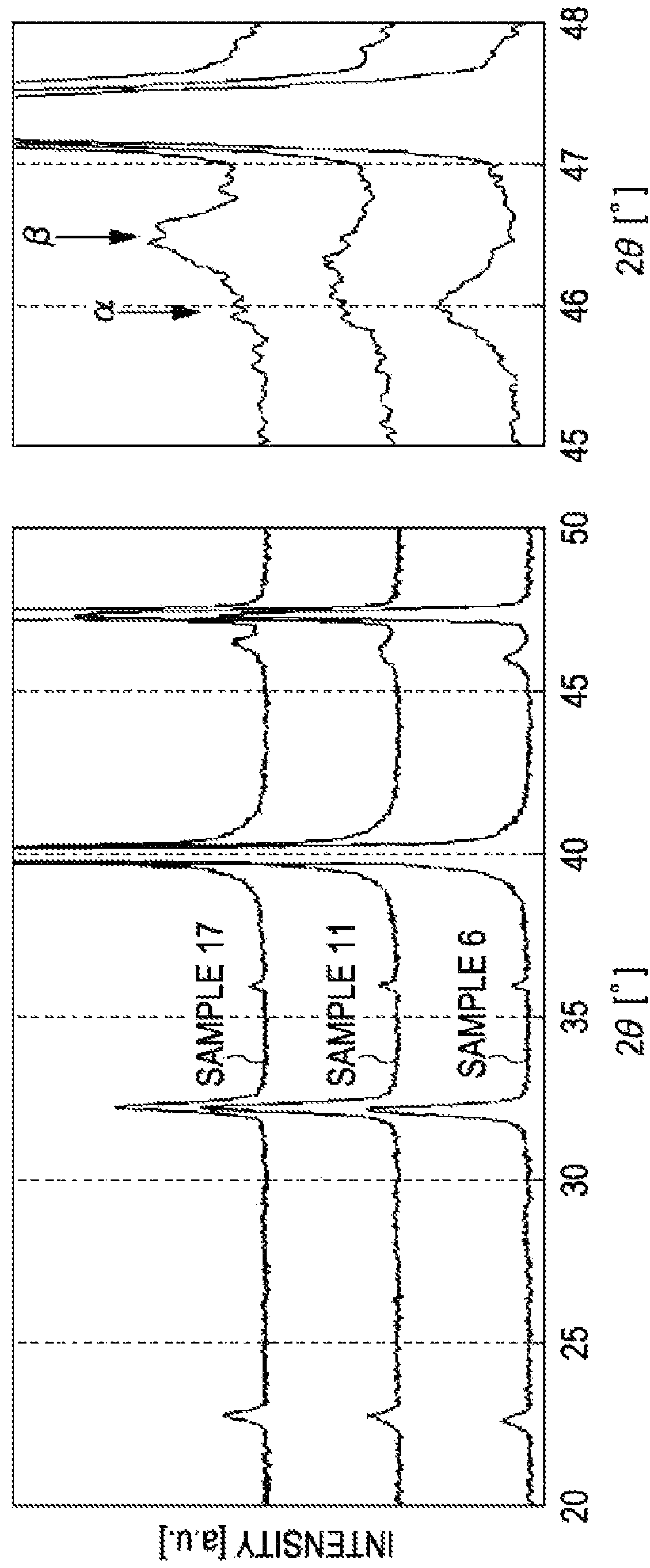


FIG. 17

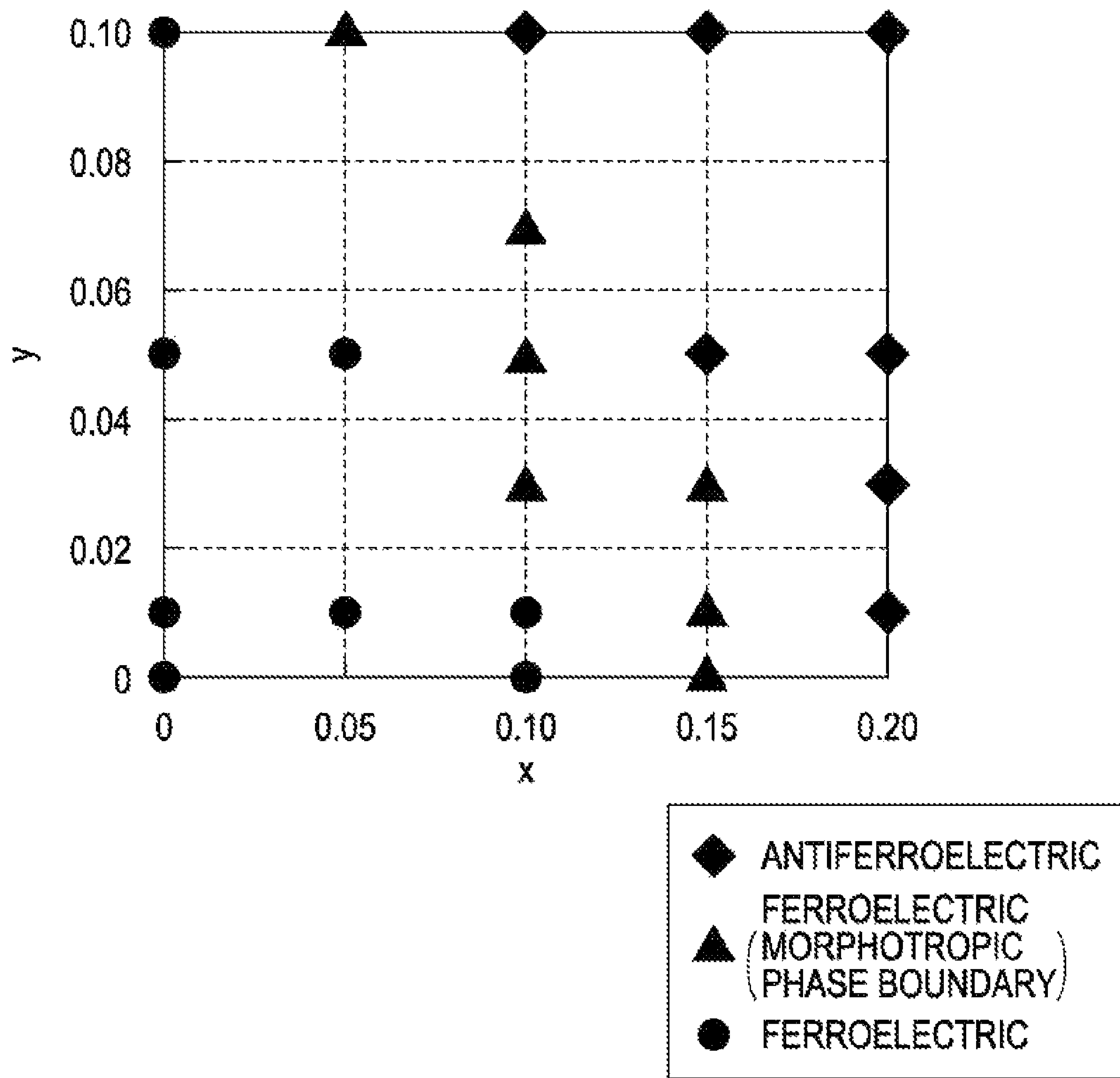


FIG. 18A

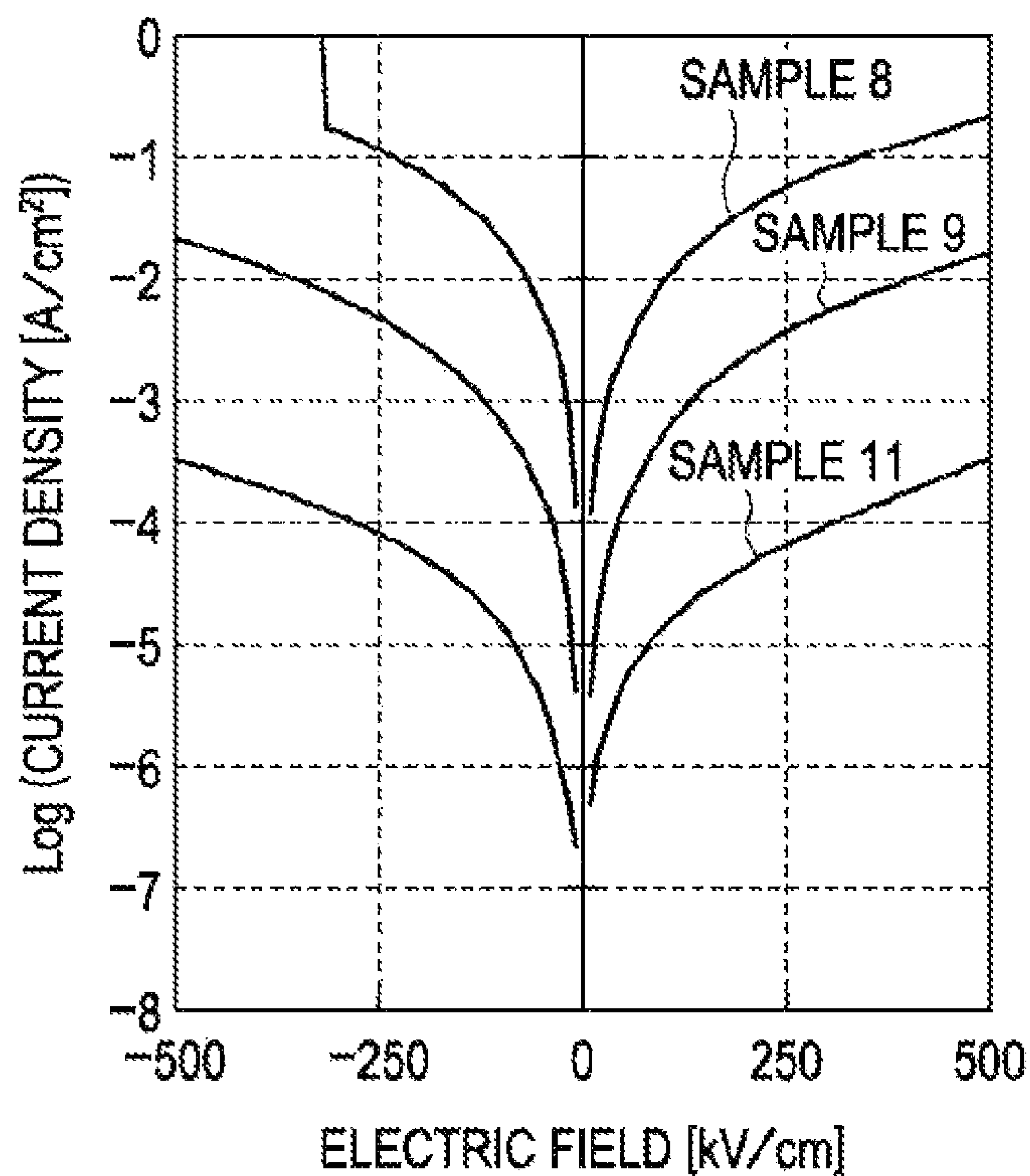


FIG. 18B

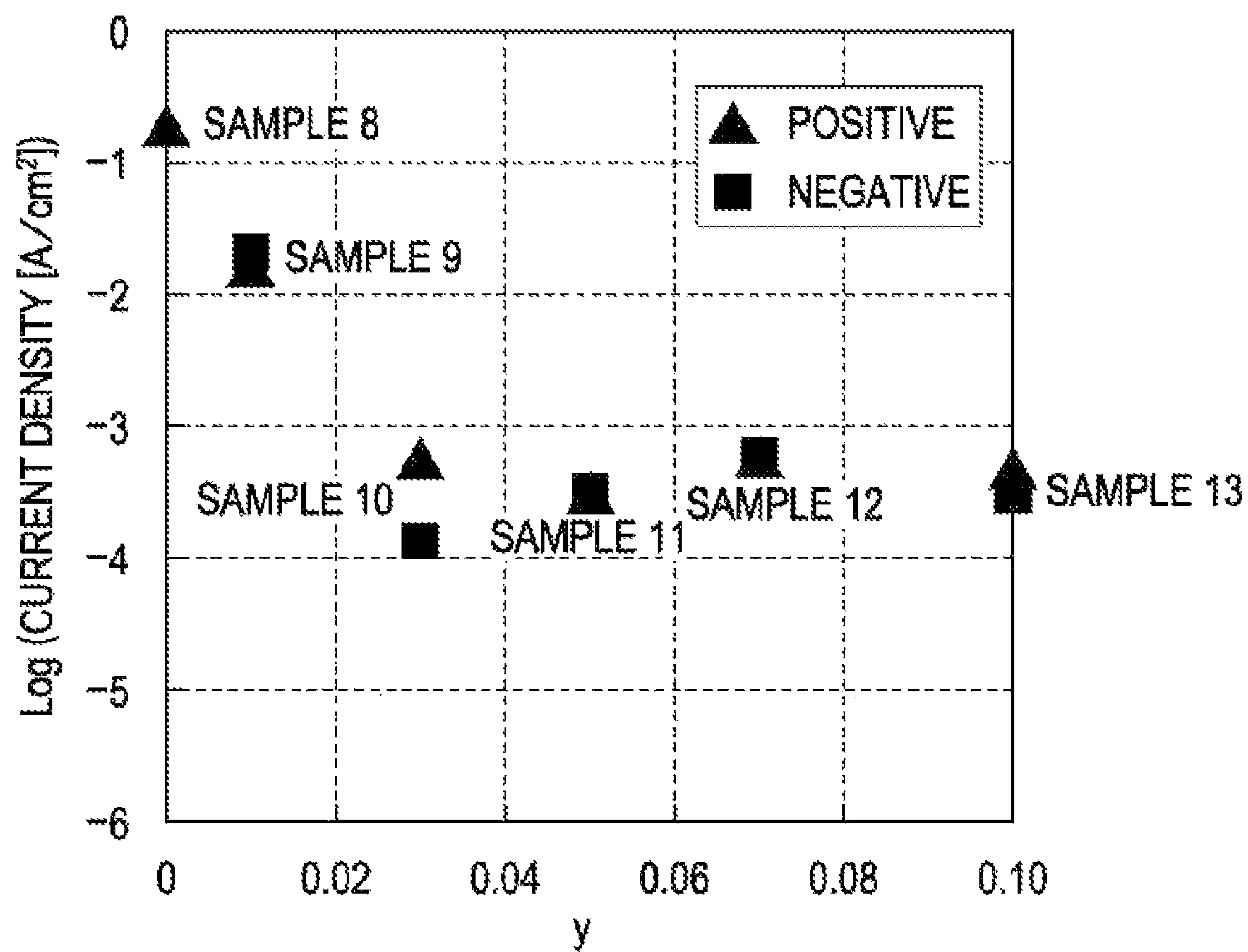


FIG. 19A

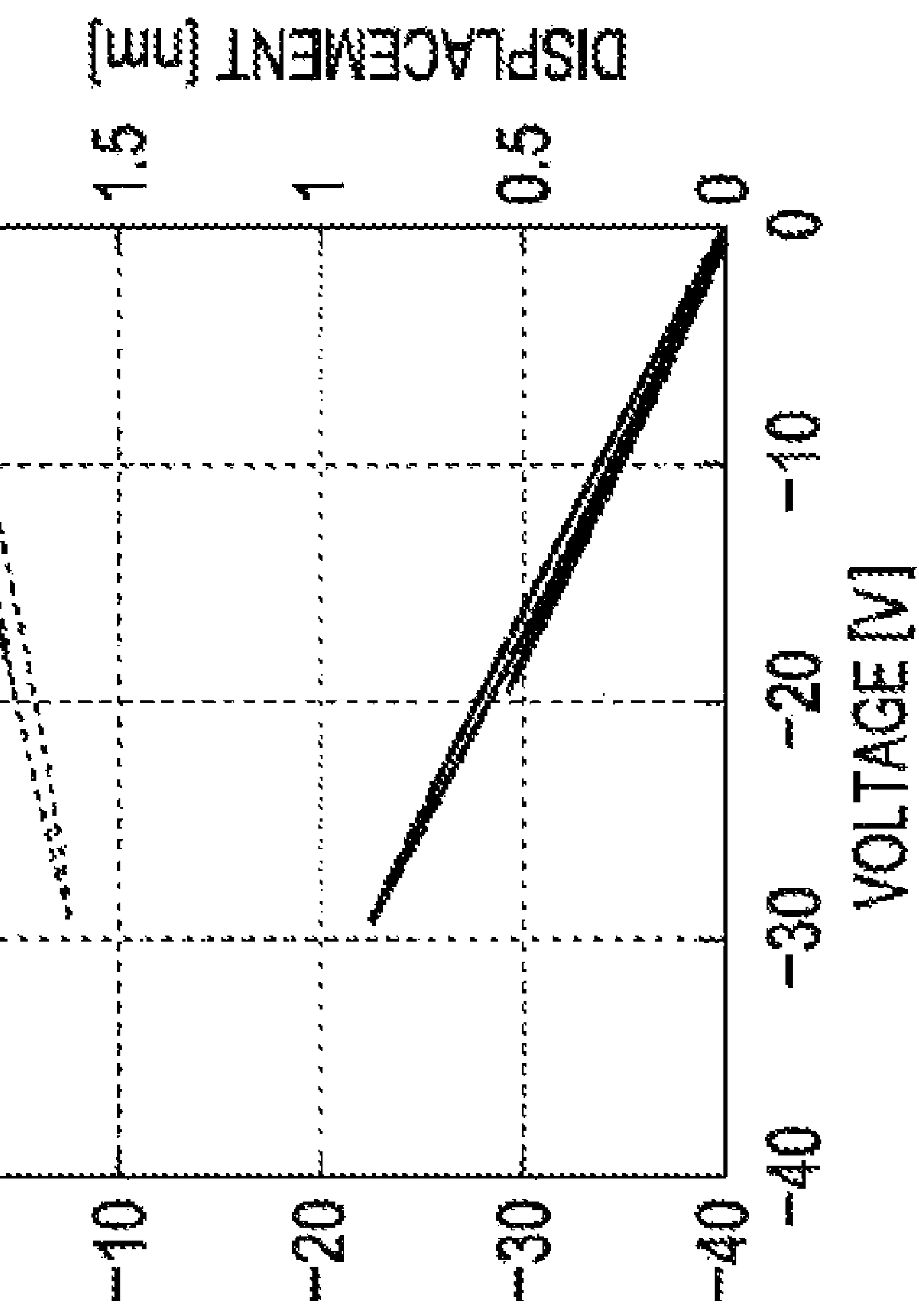


FIG. 19B

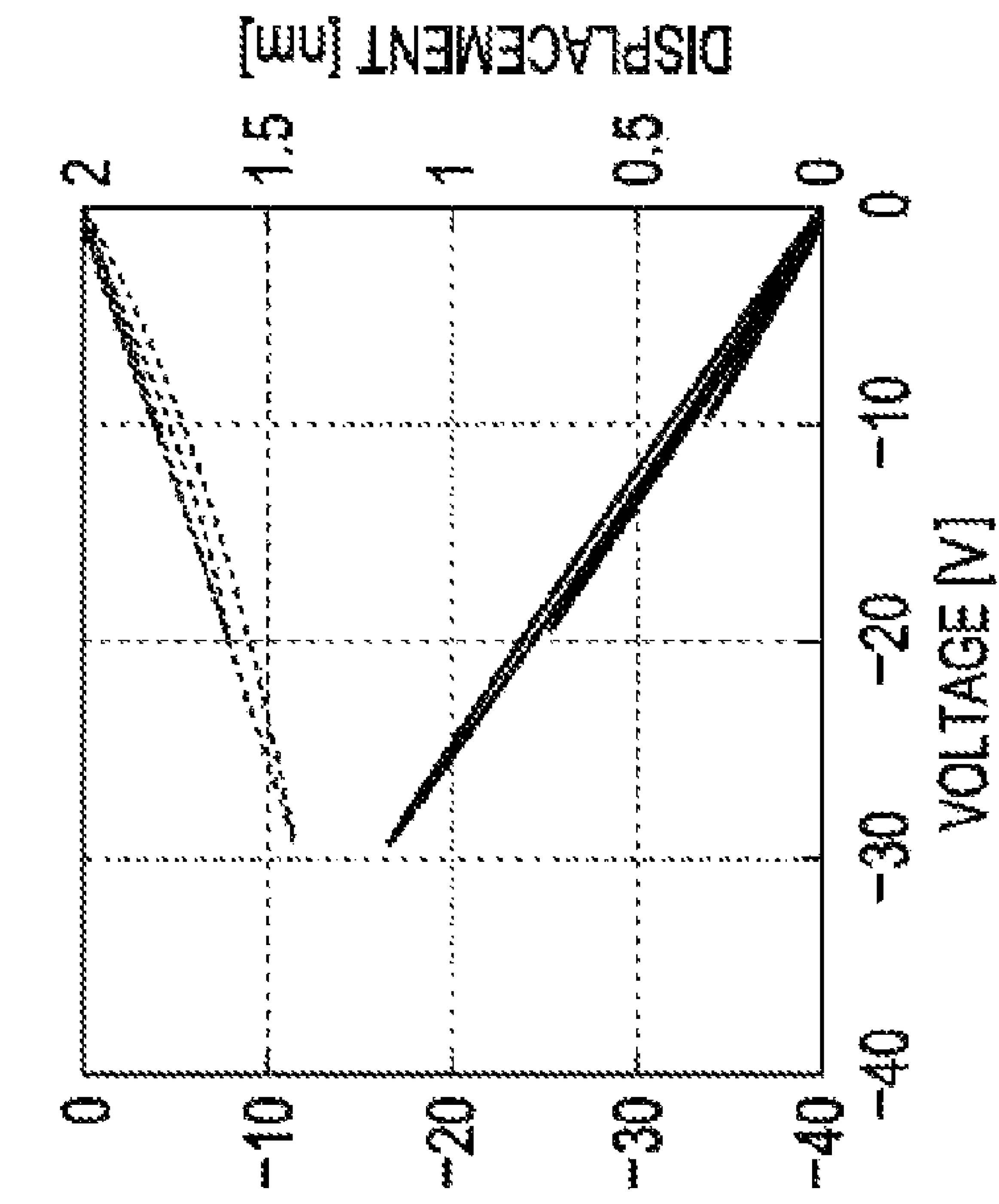


FIG. 19C

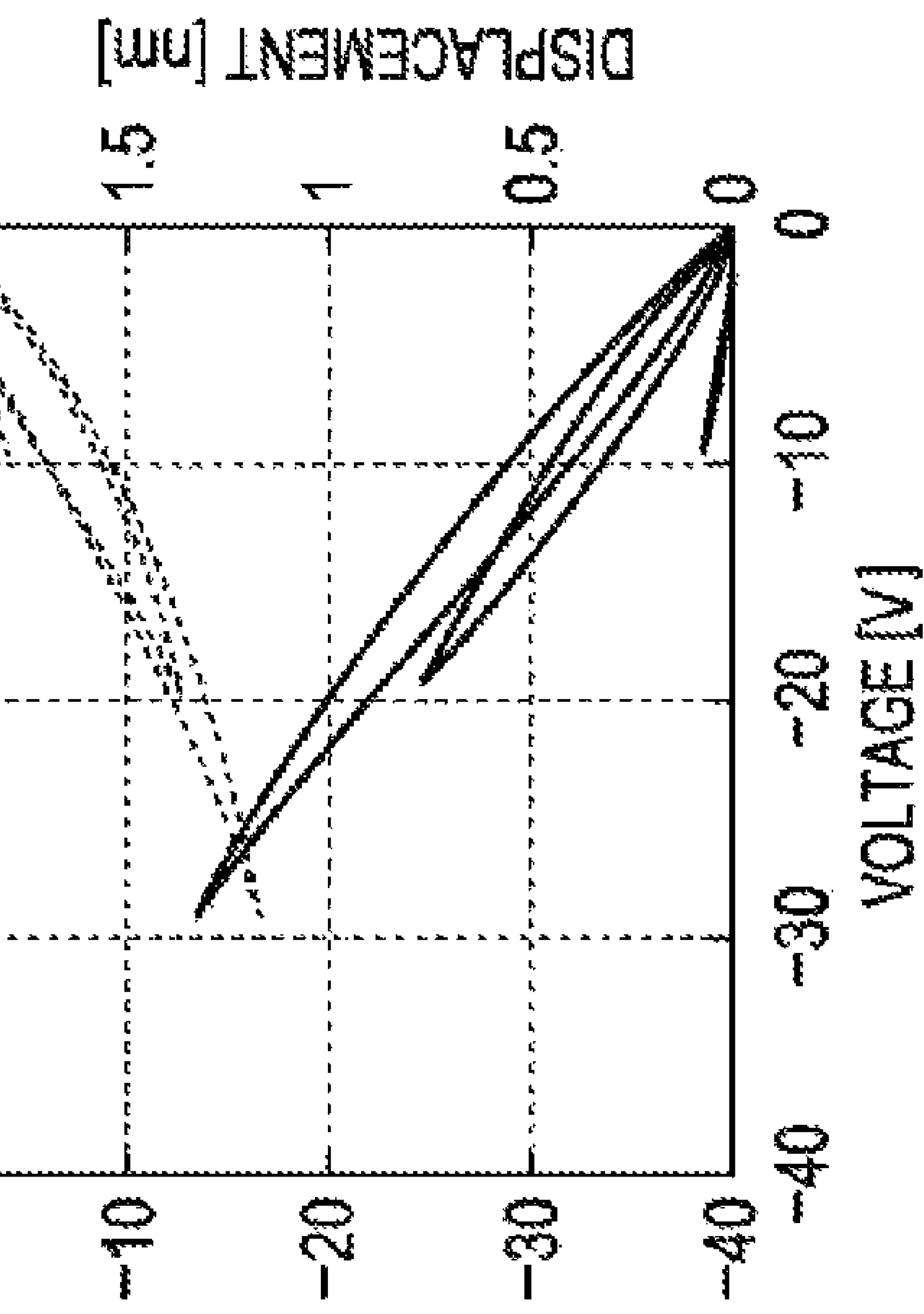


FIG. 19D

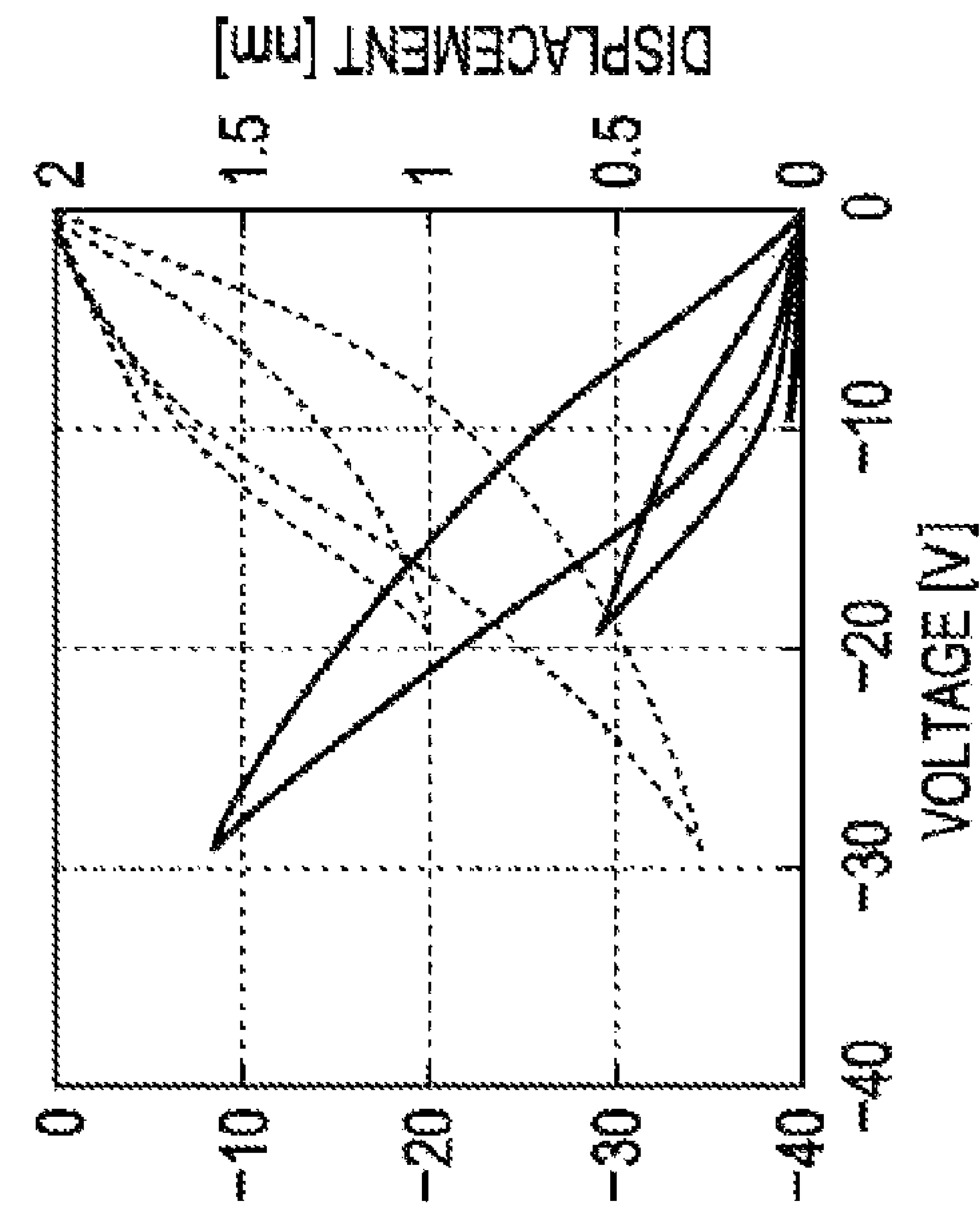
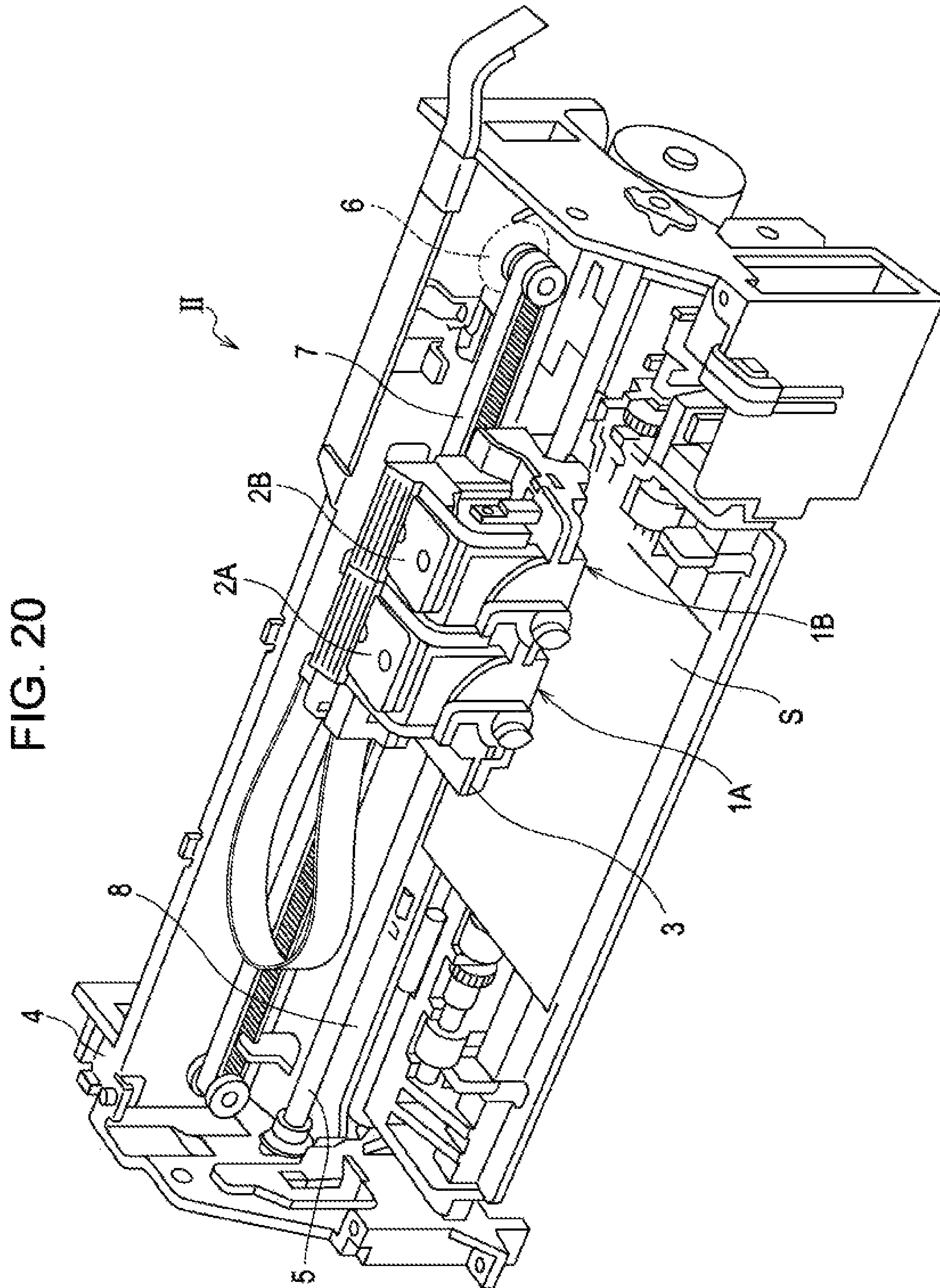


FIG. 20



LIQUID EJECTION HEAD

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. application Ser. No. 13/046,671 filed on Mar. 11, 2011, which claims the benefit of priority to Japanese Patent Application No. 2010-056806 filed Mar. 12, 2010, and Japanese Patent Application No. 2010-122800 filed May 28, 2010, the contents of which are hereby incorporated by reference in their entireties.

BACKGROUND

1. Technical Field

The present invention relates to a liquid ejection head having a piezoelectric element that causes a pressure change in a pressure generating chamber communicating with a nozzle opening and has a piezoelectric layer and an electrode for applying a voltage to the piezoelectric layer, a liquid ejection device, a piezoelectric element, and a piezoelectric material.

2. Related Art

Mentioned as piezoelectric elements for use in liquid ejection heads is a piezoelectric element having a structure where a piezoelectric material that exhibits an electromechanically conversion function, such as a piezoelectric layer containing a crystallized dielectric material, is sandwiched between two electrodes. Such a piezoelectric element is mounted on a liquid ejection head as, for example, an actuator device in a bending vibration mode. Mentioned as a typical example of the liquid ejection head is, for example, an ink jet recording head in which a part of a pressure generation chamber communicating with a nozzle opening for discharging ink droplets is constituted by a diaphragm and which discharges ink in the pressure generation chamber as ink droplets from the nozzle opening by deforming the diaphragm by the piezoelectric element to pressurize the ink. Mentioned as the piezoelectric element to be mounted on such an ink jet recording head is, for example, a piezoelectric element formed by forming a uniform piezoelectric material layer throughout the entire surface of the diaphragm by a film formation technique, and then cutting the piezoelectric material layer into a shape corresponding to the pressure generation chamber by a lithography method to be independent for every pressure generation chamber.

The piezoelectric material for use in such a piezoelectric element is required to have high piezoelectric characteristics (distortion level), and lead zirconate titanate (PZT) is mentioned as a typical example (JP-A-2001-223404).

However, a piezoelectric material in which the lead content is reduced has been desired from the viewpoint of environmental problems. Examples of piezoelectric materials not containing lead include $BiFeO_3$ which is a perovskite type complex oxide represented by, for example, ABO_3. Such a $BiFeO_3$-based piezoelectric material containing Bi and Fe has problems in that the insulation properties are low and a leakage current occurs. Such problems similarly occur in other piezoelectric elements without being limited to the liquid ejection head typified by the ink jet recording head.

SUMMARY

An advantage of some aspects of the invention is to provide a liquid ejection head having a piezoelectric element that has high insulation properties, can suppress the generation of a leakage current, and has a reduced environmental load, a liquid ejection device, a piezoelectric element, and a piezoelectric material.

According to a first aspect of the invention that solves the above-described problems is a liquid ejection head having a pressure generation chamber communicating with a nozzle opening and a piezoelectric element having a piezoelectric layer and an electrode provided on the piezoelectric layer, in which the piezoelectric layer is a perovskite type complex oxide containing bismuth, iron, and cerium and the piezoelectric layer contains the cerium in a proportion of 0.01 or more and 0.13 or lower in a molar ratio based on the total amount of the bismuth and the cerium.

According to such an aspect, by the use of the piezoelectric material containing a perovskite type complex oxide containing iron and bismuth and a given proportion of cerium for the piezoelectric layer, high insulation properties can be obtained and the generation of a leakage current can be suppressed. Moreover, since the lead content can be reduced, a load to the environment can be reduced.

The piezoelectric layer may further contain lanthanum. According to this aspect, a liquid ejection head having a piezoelectric material that can become a ferroelectric or an antiferroelectric exhibiting an electric field-induced phase transition while maintaining the effects of obtaining high insulation properties and suppressing the generation of a leakage current is obtained. Moreover, a hetero-phase derived from bismuth ferrate can be suppressed.

The piezoelectric layer contains the lanthanum in a proportion of 0.05 or more and 0.20 or lower in a molar ratio based on the total amount of the bismuth, the cerium, and the lanthanum. According to this aspect, a liquid ejection head having a piezoelectric material of a ferroelectric or an antiferroelectric exhibiting an electric field-induced phase transition in accordance with the lanthanum amount is achieved.

The piezoelectric layer may exhibit an electric field-induced phase transition. According to this aspect, a liquid ejection head having a piezoelectric element having a high distortion level can be achieved.

The piezoelectric layer may be a ferroelectric. According to this aspect, a liquid ejection head having a piezoelectric element in which the distortion level is easily controlled, and, for example, the size of droplets to be discharged is easily controlled can be achieved.

It is preferable that, in the piezoelectric layer, a diffraction peak belonging to a phase exhibiting ferroelectricity and a diffraction peak belonging to a phase exhibiting antiferroelectricity be simultaneously observed in a powder X-ray diffraction pattern. According to this aspect, a piezoelectric element having a high distortion level can be obtained due to the presence of a Morphotropic phase boundary (M. P. B.) of an antiferroelectric phase and a ferroelectric phase.

According to a seventh aspect, a liquid ejection device has the liquid ejection head of the aspects described above. According to such an aspect, a liquid ejection device in which dielectric breakdown is prevented and the reliability is excellent is obtained because the liquid ejection device has a liquid ejection head having high insulation properties and capable of suppressing the generation of a leakage current. In addition, a liquid ejection device in which the lead content is reduced and a load to the environment is reduced can be provided.

According to an eighth aspect of the invention, a piezoelectric element has a piezoelectric layer and an electrode provided on the piezoelectric layer, in which the piezoelectric layer is a perovskite type complex oxide containing bismuth, iron, and cerium and the piezoelectric layer contains the

cerium in a proportion of 0.01 or more and 0.13 or lower in a molar ratio based on the total amount of the bismuth and the cerium. According to the aspect, high insulation properties can be obtained and the generation of a leakage current can be suppressed by the use of a piezoelectric material containing a perovskite type complex oxide containing iron and bismuth and a given ratio of cerium for the piezoelectric layer. Moreover, since the lead content can be reduced, a load to the environment can be reduced.

According to a ninth aspect of the invention, a piezoelectric material which is a perovskite type complex oxide containing bismuth, iron, and cerium and which contains the cerium in a proportion of 0.01 or more and 0.13 or lower in a molar ratio based on the total amount of the bismuth and the cerium. According to the aspect, a piezoelectric material in which the insulation properties are high and the generation of a leakage current can be suppressed is obtained. Moreover, since the lead content can be reduced, a load to the environment can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described with reference to the accompanying drawings, wherein like numbers reference like elements.

FIG. **1** is an exploded perspective view schematically illustrating the structure of a recording head according to a first embodiment.

FIG. **2** is a plan view of the recording head according to the first embodiment.

FIG. **3** is a cross sectional view of the recording head according to the first embodiment.

FIG. **4** is a diagram illustrating the P-V hysteresis of an antiferroelectric.

FIGS. **5**A and **5**B are cross sectional views illustrating a process for manufacturing the recording head according to the first embodiment.

FIGS. **6**A to **6**C are cross sectional views illustrating the process for manufacturing the recording head according to the first embodiment.

FIGS. **7**A and **7**B are cross sectional views illustrating the process for manufacturing the recording head according to the first embodiment.

FIGS. **8**A to **8**C are cross sectional views illustrating the process for manufacturing the recording head according to the first embodiment.

FIGS. **9**A and **9**B are cross sectional views illustrating the process for manufacturing the recording head according to the first embodiment.

FIGS. **10**A to **10**D are views illustrating the P-E curve of samples 1 to 4.

FIG. **11** is a diagram illustrating the X ray diffraction pattern of the samples 1 to 4.

FIG. **12** is a diagram illustrating the J-E Curve of the samples 1 to 4.

FIG. **13** is a diagram illustrating the S-V curve of the sample 1.

FIGS. **14**A to **14**D are diagrams illustrating the P-E curve of the samples 6, 11, 17, and 21.

FIG. **15** is a diagram illustrating the X ray diffraction pattern of the samples 2 and 11.

FIGS. **16**A and **16**B are diagrams illustrating the X ray diffraction pattern of the samples 6, 11, and 17.

FIG. **17** is a diagram in which the analysis results of the X ray diffraction pattern are plotted against the composition.

FIGS. **18**A to **18**B are diagram s illustrating the measurement results of the J-E Curve.

FIGS. **19**A to **19**D are diagram s illustrating the S-V curve of the samples 6, 11, 17, and 21.

FIG. **20** is a view schematically illustrating the structure of a recording device according to one embodiment of the invention.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

First Embodiment

FIG. **1** is an exploded perspective view schematically illustrating the structure of an ink jet recording head which is one example of a liquid ejection head according to a first embodiment of the invention, FIG. **2** is a plan view of FIG. **1**, and FIG. **3** is a cross sectional view along the III-III line of FIG. **2**. As illustrated in FIGS. **1** to **3**, a flow path forming substrate **10** of this embodiment contains a silicon single crystal substrate, on one surface of which an elastic film **50** containing silicon dioxides is formed.

In the flow path forming substrate **10**, two or more pressure generation chambers **12** are arranged in parallel in the width direction thereof. In an outside region in the longitudinal direction of the pressure generation chambers **12** of the flow path forming substrate **10**, a communication portion **13** is formed and the communication portion **13** and each pressure generation chamber **12** are communicated with each other through an ink supply path **14** and a communication path **15** provided for every pressure generation chamber **12**. The communication portion **13** communicates with a reservoir portion **31** of a protective substrate described later to constitute a part of a reservoir to serve as a common ink chamber of the respective pressure generation chambers **12**. The ink supply path **14** is formed with a narrower width than that of the pressure generation chamber **12** and keeps the flow path resistance of ink flowing into the pressure generation chamber **12** from the communication portion **13** at a constant rate. In this embodiment, the ink supply path **14** is formed by narrowing the width of the flow path from one side but the ink supply path may be formed by narrowing the width of the flow path from both sides. The ink supply path may be formed by narrowing in the thickness direction instead of narrowing the width of the flow path. In this embodiment, the flow path forming substrate **10** is provided with a liquid flow path constituted by the pressure generation chambers **12**, the communication portion **13**, the ink supply paths **14**, and the communication paths **15**.

To the opening surface side of the flow path forming substrate **10**, a nozzle plate **20** in which nozzle openings **21** each communicating with the vicinity of the end of each pressure generation chamber **12** opposite to the ink supply paths **14** are formed is adhered with an adhesive, a thermally welding film, or the like. The nozzle plate **20** contains glass ceramics, a silicon single crystal substrate, stainless steel, or the like, for example.

In contrast, on the side opposite to the opening surface of such a flow path forming substrate **10**, the elastic film **50** is formed as described above. On the elastic film **50**, an adhesion layer **56** containing titanium oxide for increasing the adhesion of the elastic film **50** or the like with the base of a first electrode **60** is provided. On the elastic film **50**, an insulator film containing zirconium dioxide or the like may be provided as required.

Furthermore, on the adhesion layer **56**, the first electrode **60**, a piezoelectric layer **70** which is a thin film having a thickness of 2 μm or lower and preferably 1 to 0.3 μm, and a second electrode **80** are laminated to constitute a piezoelec-

tric element **300**. Here, the piezoelectric element **300** refers to a portion containing the first electrode **60**, the piezoelectric layer **70**, and the second electrode **80**. In general, any one of the electrodes of the piezoelectric elements **300** is used as a common electrode and the other electrodes and the piezoelectric layers **70** are formed by patterning for every pressure generation chamber **12**. In this embodiment, the first electrode **60** is used as the common electrode of the piezoelectric elements **300** and the second electrode **80** is used as an individual electrode of the piezoelectric elements **300** but the electrodes may be used in an opposite manner depending on a drive circuit or wiring. Here, a combination of the piezoelectric element **300** and a diaphragm in which displacement arises by the drive of the piezoelectric element **300** is referred to as an actuator device. In the above-described example, the elastic film **50**, the adhesion layer **56**, the first electrode **60**, and the insulator film provided as required act as the diaphragm. However, it is a matter of fact that the invention is not limited to the example and the elastic film **50** or the adhesion layer **56** may not be provided, for example. The piezoelectric element **300** may substantially serve as the diaphragm.

In this embodiment, a piezoelectric material constituting the piezoelectric layer **70** is a perovskite type complex oxide containing bismuth, iron, and cerium. On the A site of the perovskite type complex oxide, i.e., an ABO_3 type complex oxide, twelve oxygens are coordinated and, on the B site, six oxygens are coordinated to form an octahedron. On the A site, bismuth (Bi) and cerium (Ce) are positioned and, on the B site, iron (Fe) is positioned. More specifically, the perovskite type complex oxide containing bismuth, iron, and cerium is presumed to have a structure where a part of Bi of bismuth ferrate is replaced by Ce.

In this embodiment, in the perovskite type complex oxide containing bismuth, iron, and cerium, Ce is contained in a proportion of 0.01 or more and 0.13 or lower in a molar ratio based on the total amount of Bi and Ce.

Thus, when the perovskite type complex oxide containing bismuth, iron, and cerium is used as the piezoelectric material constituting the piezoelectric layer **70** and the proportion of the cerium is adjusted to be 0.01 or more and 0.13 or lower in a molar ratio based on the total amount of the bismuth and the cerium, the insulation properties can be made high and a leakage current can be suppressed as compared with a piezoelectric material not containing Ce, i.e., a $BiFeO_3$ type piezoelectric material containing Bi and Fe and not containing Ce as shown in Examples described later. It is a matter of course that since the lead content can be reduced, a load to the environment can be reduced. For example, the piezoelectric layer **70** in which a leakage current when a 500 $kVcm^{-1}$ electric field is applied is equal to or lower than 1.0×10^{-1} Acm^{-2} can be achieved.

The piezoelectric layer **70** may further contain lanthanum (La). By the use of a perovskite type complex oxide containing bismuth, iron, cerium, and lanthanum, a piezoelectric material that can become a ferroelectric or an antiferroelectric exhibiting an electric field-induced phase transition. The perovskite type complex oxide containing bismuth, iron, cerium, and lanthanum is presumed to have a structure where a part of Bi of bismuth ferrate is replaced by Ce and La.

It is a matter of course that even in the case of a piezoelectric material further containing La, the effects of increasing the insulation properties to a high degree and suppressing a leakage current can also be maintained. The La content is not limited and may be adjusted to be, for example, 0.05 or more and 0.20 or lower in a molar ratio based on the total amount of Bi, Ce, and La.

Here, the electric field-induced phase transition is a phase transition caused by an electric field and refers to a phase transition from an antiferroelectric phase to a ferroelectric phase or a phase transition from a ferroelectric phase to an antiferroelectric phase. The ferroelectric phase refers to a state where the polarization axes are oriented in the same direction and the antiferroelectric phase refers to a state where the polarization axes are oriented in the opposite direction. For example, the phase transition from an antiferroelectric phase to a ferroelectric phase refers to a state where the polarization axes oriented in the opposite direction of the antiferroelectric phase rotate 180°, so that the polarization axes are oriented in the same direction to convert the phase to a ferroelectric phase. A distortion caused by expansion or contraction of a lattice due to such an electric field-induced phase transition is an electric field-induced phase transition distortion caused by the electric field-induced phase transition.

A substance exhibiting such an electric field-induced phase transition is the antiferroelectric. In other words, a substance in which the polarization axes are oriented in the opposite direction in a state where there is no electric field and the polarization axes rotate by an electric field to be oriented in the same direction is the antiferroelectric. Such an antiferroelectric exhibits a double hysteresis having two hysteresis loop shapes in a positive electric field direction and a negative electric field direction as illustrated in FIG. **4** illustrating one example of the P-V curve representing the relationship between the polarization P and the voltage V of the antiferroelectric. In FIG. **4**, the regions VF and VAF where the polarization rapidly changes are portions where the phase transition from the ferroelectric phase to the antiferroelectric phase or the phase transition from the ferroelectric phase to the antiferroelectric phase occurs. Unlike the antiferroelectric, the ferroelectric exhibits a hysteresis curve in the P-V curve, in which the distortion level linearly changes to an applied voltage by orienting the polarization direction to one direction.

In contrast, in the antiferroelectric, the P-V curve does not exhibit a double hysteresis which is observed in the antiferroelectric and the distortion level linearly changes to an applied voltage by orienting the polarization direction to one direction. Thus, since the distortion level is easily controlled, the size of droplets to be discharged is easily controlled, and both a small-amplitude vibration that causes a slight vibration and a large-amplitude vibration that generates a large excluded volume can be generated by one piezoelectric element.

In the case of the ferroelectric, when the piezoelectric layer **70** is subjected to powder X-ray diffraction measurement, the diffraction peak belonging to a phase exhibiting ferroelectricity (ferroelectric phase) is observed in the diffraction pattern. It is preferable that the diffraction peak belonging to the phase exhibiting ferroelectricity (ferroelectric phase) and the diffraction peak belonging to a phase exhibiting antiferroelectricity (antiferroelectric phase) be simultaneously observed. Thus, in the case of the piezoelectric layer **70** in which the diffraction peak belonging to the phase exhibiting ferroelectricity and the diffraction peak belonging to the phase exhibiting antiferroelectricity are simultaneously observed, i.e., exhibiting the Morphotropic phase boundary (M. P. B.) of the antiferroelectric phase and the ferroelectric phase, a piezoelectric element having a high distortion level can be achieved among ferroelectrics. The diffraction peak belonging to the phase exhibiting ferroelectricity is observed near 2θ=46° when powder X-ray diffraction measurement is carried out, for example. The diffraction peak belonging to the phase

exhibiting antiferroelectricity is observed near 2θ=46.5° when powder X-ray diffraction measurement using a CuKα line as the X-ray source is carried out, for example. These diffraction peak positions are dependent on planar spacing and a shift in the diffraction peak position may occur due to changes in a stress from a substrate or the outside depending on a creation method, shape, external stress, or the like. In contrast, in the antiferroelectric, the diffraction peak belonging to the phase exhibiting ferroelectricity is not observed and only the diffraction peak belonging to the phase exhibiting antiferroelectricity is observed.

When the piezoelectric layer **70** contains La, a heterophase derived from bismuth ferrate can be suppressed.

To each of the second electrodes **80** which are individual electrodes of such piezoelectric elements **300**, a lead electrode **90** containing gold (Au) or the like, for example, which is drawn from the vicinity of the end at the ink supply path **14** side to be extended onto the elastic film **50** or the insulator film provided as required.

On the flow path forming substrate **10** on which such piezoelectric elements **300** are formed, i.e., on the first electrode **60**, the elastic film **50**, the insulator film provided as required, and the lead electrode **90**, a protective substrate **30** having the reservoir portion **31** constituting at least one part of a reservoir **100** is joined through an adhesive **35**. The reservoir portion **31** is formed penetrating the protective substrate **30** in the thickness direction and in the width direction of the pressure generation chamber **12** and is communicated with the communication portion **13** of the flow path forming substrate **10** as described above to constitute the reservoir **100** to serve as a common ink chamber of the respective pressure generation chambers **12** in this embodiment. Or, the communication portion **13** of the flow path forming substrate **10** may be divided into two or more portions for every pressure generation chamber **12**, so that only the reservoir portion **31** may be used as a reservoir. Or, only the pressure generation chambers **12** may be provided in the flow path forming substrate **10** and the ink supply path **14** communicating with the reservoir **100** and the respective pressure generation chambers **12** may be provided to a member (e.g., the elastic film **50** or the insulator film provided as required) provided between the flow path forming substrate **10** and the protective substrate **30**, for example.

At a region facing the piezoelectric elements **300** of the protective substrate **30**, a piezoelectric element holding portion **32** having a space so as not to impede the movement of the piezoelectric elements **300** is provided. The piezoelectric element holding portion **32** may have a space so as not to impede the movement of the piezoelectric elements **300** and the space may be sealed or may not be sealed.

As such a protective substrate **30**, it is preferable to use materials having substantially the same coefficient of thermal expansion as that of the flow path forming substrate **10**, such as glass and ceramic materials. In this embodiment, the protective substrate **30** is formed using a silicon single crystal substrate which is the same material as that of the flow path forming substrate **10**.

In the protective substrate **30**, a penetration hole **33** penetrating the protective substrate **30** in the thickness direction is provided. The vicinity of the end of the lead electrode **90** drawn from each of the piezoelectric elements **300** is provided in such a manner as to be exposed in the penetration hole **33**.

On the protective substrate **30**, a drive circuit **120** for driving the piezoelectric elements **300** arranged in parallel is fixed. As the drive circuit **120**, a circuit substrate, a semiconductor integrated circuit (IC), or the like can be used, for example. The drive circuit **120** and the lead electrode **90** are electrically connected to each other through a connection wiring **121** containing a conductive wire, such as a bonding wire.

Onto such a protective substrate **30**, a compliance substrate **40** containing a sealing film **41** and a fixing plate **42** is joined. Here, the sealing film **41** contains materials having low rigidity and flexibility. One area of the reservoir portion **31** is sealed with the sealing film **41**. The fixing plate **42** is formed with a relatively hard material. A region facing the reservoir **100** of the fixing plate **42** is an opening portion **43** completely opening in the thickness direction. Thus, one are of the reservoir **100** is sealed only by the sealing film **41** having flexibility.

In such an ink jet recording head I of this embodiment, an ink is taken from an ink introduction port connected to an ink supply member (not illustrated) at the outside, the inside thereof from the reservoir **100** to the nozzle opening **21** is filled with the ink, and a voltage is applied between the first electrode **60** and the second electrode **80** corresponding to each of the pressure generation chambers **12** in accordance with a record signal from the drive circuit **120** to bend and deform the elastic film **50**, the adhesion layer **56**, the first electrode **60**, and the piezoelectric layer **70** to thereby increase the pressure in each of the pressure generation chamber **12**, whereby ink droplets are discharged from the nozzle openings **21**.

Next, one example of a method for manufacturing the ink jet recording head of this embodiment will be described with reference to FIGS. **5** to **9**. FIGS. **5** to **9** are cross sectional views in the longitudinal direction of the pressure generation chamber.

First, as illustrated in FIG. **5**A, a silicon dioxide film containing silicon dioxide (SiO_2) or the like constituting the elastic film **50** is formed on the surface of a flow path forming substrate wafer **110** which is a silicon wafer by thermal oxidation or the like. Subsequently, as illustrated in FIG. **5**B, the adhesion layer **56** containing titanium oxide or the like is formed by a reactive sputtering method, thermal oxidation, or the like, on the elastic film **50** (silicon dioxide film).

Next, as illustrated in FIG. **6**A, the first electrode **60** containing platinum, iridium, iridium oxide, or a laminate thereof is formed on the entire surface of the adhesion layer **56** by a sputtering method or the like.

Subsequently, the piezoelectric layer **70** is laminated on the first electrode **60**. Methods for manufacturing the piezoelectric layer **70** are not limited. For example, the piezoelectric layer **70** can be formed by a chemical solution method, such as an MOD (Metal-Organic Decomposition) method including applying a solution in which an complex is dissolved and dispersed in a solvent and drying the same, and then firing the same at a high temperature to thereby obtain the piezoelectric layer **70** or a sol-gel method. In addition, a laser ablation method, a sputtering method, a pulsed laser deposition method (PLD method), a CVD method, an aerosol deposition method, and the like may be used.

A specific example of a procedure for forming the piezoelectric layer **70** is as follows. First, as illustrated in FIG. **6**B, a sol or an MOD solution (precursor solution) containing an complex, specifically, an complex containing Bi, Ce, and Fe, and La, which is blended as required at a target ratio is applied onto the first electrode **60** using a spin coating method or the like to thereby form the piezoelectric precursor film **71** (application process).

The precursor solution to be applied is obtained by mixing complexes containing each of Bi, Ce, Fe, and La so that the molar ratio of each metal becomes a desired molar ratio, and

then dissolving or dispersing the mixture using an organic solvent, such as alcohol. As the complexes containing each of Bi, Ce, Fe, and La, a metal alkoxide, an organic acid salt, a β diketone complex, and the like can be used, for example. Examples of the complex containing Bi include 2-ethylhexanoic acid bismuth. Examples of the complex containing Fe include 2-ethylhexanoic acid iron. Examples of the complex containing Ce include 2-ethyl hexanoic acid cerium. Examples of the complex containing La include 2-ethyl hexanoic acid lanthanum.

Subsequently, the piezoelectric precursor film **71** is heated to a given temperature, and is dried for a defined period of time (drying process). Next, the dried piezoelectric precursor film **71** is degreased by heating the same to a given temperature, and holding the same for a defined period of time (degreasing process). The degreasing process as used herein refers to a process for removing the organic ingredients contained in the piezoelectric precursor film **71** as NO_2, CO_2, H_2O, or the like, for example. The atmosphere of the drying process or the degreasing process is not limited and the processes may be carried out in the air or inactive gas.

Next, as illustrated in FIG. **6**C, the piezoelectric precursor film **71** is crystallized by heating the same to a given temperature, e.g., about 600 to 700° C., and holding the same for a defined period of time to form the piezoelectric film **72** (firing process). Also in the firing process, the atmosphere is not limited and the process may be carried out in the air or inactive gas.

Examples of heating devices for use in the drying process, the degreasing process, and the firing process include an RTA (Rapid Thermal Annealing) device that performs heating by irradiation of an infrared lamp or a hot plate.

Next, as illustrated in FIG. **7**A, on the piezoelectric film **72**, the first electrode **60** and a first layer of the piezoelectric film **72** are simultaneously patterned using a resist having a given shape (not illustrated) as a mask so that the sides thereof incline.

Subsequently, the resist is separated, and then the application process, the drying process, and the degreasing process described above or an application process, a drying process, a degreasing process, and a firing process are repeated two or more times in accordance with a desired film thickness or the like to form the piezoelectric layer **70** containing two or more of the piezoelectric films **72**, thereby forming the piezoelectric layer **70** containing two or more of the piezoelectricity film **72** and having a given thickness as illustrated in FIG. **7**B. For example, when the film thickness per application of the coating solution is about 0.1 μm, the film thickness of the entire piezoelectric layer **70** containing ten layers of the piezoelectric films **72** is about 1.1 μm, for example. In this embodiment, the piezoelectric film **72** is provided by lamination but the piezoelectric film **72** may contain only one layer.

After forming the piezoelectric layer **70** as described above, as illustrated in FIG. **8**A, the second electrode **80** containing platinum or the like is formed by a sputtering method or the like on the piezoelectric layer **70**, and the piezoelectric layer **70** and the second electrode **80** are simultaneously patterned in a region facing each of the pressure generation chambers **12**, thereby forming the piezoelectric element **300** containing the first electrode **60**, the piezoelectric layer **70**, and the second electrode **80**. The patterning of the piezoelectric layer **70** and the second electrode **80** can be carried out at once by carrying out by dry etching through a resist (not illustrated) formed into a given shape. Thereafter, post-annealing may be carried out in a temperature range (600° C. to 700° C.) as required. Thus, a favorable interface of the piezoelectric layer **70** and the first electrode **60** or the second electrode **80** can be formed and the crystallinity of the piezoelectric layer **70** can be improved.

Next, as illustrated in FIG. **8**B, patterning is carried out for every piezoelectric element **300** through a mask pattern (not illustrated) containing, for example, a resist or the like on the entire surface of the flow path forming substrate wafer **110** after the formation of the lead electrode **90** containing gold (Au), for example. Next, as illustrated in FIG. **8**C, a protective substrate wafer **130** which is a silicon wafer and forms two or more protective substrates **30** is joined through the adhesive **35** to the piezoelectric element **300** side of the flow path forming substrate wafer **110**, and then the thickness of the flow path forming substrate wafer **110** is reduced to a given thickness.

Next, as illustrated in FIG. **9**A, a mask film **52** is newly formed on the flow path forming substrate wafer **110**, and is patterned into a given shape. As illustrated in FIG. **9**B, by carrying out anisotropic etching (wet etching) of the flow path forming substrate wafer **110** using an alkaline solution of KOH or the like through the mask film **52**, the pressure generation chamber **12**, the communication portion **13**, the ink supply path **14**, the communication path **15**, and the like corresponding to the piezoelectric element **300** are formed.

Thereafter, unnecessary portions of the peripheral edge of the flow path forming substrate wafer **110** and the protective substrate wafer **130** are removed by cutting by dicing or the like, for example. Then, the mask film **52** on the surface opposite to the protective substrate wafer **130** of the flow path forming substrate wafer **110** is removed. Thereafter, the nozzle plate **20** in which the nozzle openings **21** are formed is joined and the compliance substrate **40** is joined to the protective substrate wafer **130**, and then the flow path forming substrate wafer **110** or the like is divided into one-chip size of the flow path forming substrate **10** or the like as illustrated in FIG. **1**, thereby obtaining the ink jet recording head I of this embodiment.

Examples

Hereinafter, the invention will be more specifically described with reference to Examples but is not limited to the following Examples.

Sample 1

First, a silicon dioxide film having a film thickness of 1070 nm was formed on the surface of a silicon (110) substrate by thermal oxidation. Next, a titanium film was formed on the silicon dioxide film by an RF sputtering method, and was thermally oxidized to form a titanium oxide film having a film thickness of 40 nm. Next, a platinum film having a film thickness of 130 nm was formed on the titanium oxide film by a DC sputtering method to be used as a first electrode oriented along (111).

Subsequently, a piezoelectric layer was formed on the first electrode by a spin coating method. The procedure is as follows. First, a xylene solution and an octane solution of 2-ethylhexanoic acid bismuth, 2-ethylhexanoic acid cerium, and 2-ethylhexanoic acid iron were mixed at a given ratio to prepare a precursor solution. The precursor solution was added dropwise onto the substrate on which the titanium oxide film and the first electrode were formed, and the substrate was rotated at 1500 rpm, thereby forming a piezoelectric precursor film (application process). Next, drying and degreasing were performed for 3 minutes at 350° C. (drying and degreasing process). The application process and the drying and degreasing process were repeated 3 times, and then firing was performed at 650° C. for 3 minutes under a nitrogen atmosphere (nitrogen flow with a flow rate of 100

cc/minute in a heating device) by Rapid Thermal Annealing (RTA) (firing process). By repeating, 3 times, a process including performing the firing process in which firing is performed at once after repeating the application process and the drying and degreasing process 3 times, i.e., performing the application processes nine times in total, a piezoelectric layer having a thickness of 564 nm as a whole was formed.

Thereafter, a platinum film having a film thickness of 100 nm was formed by a DC sputtering method as a second electrode on the piezoelectric layer, and then fired at 650° C. for 5 minutes using RTA, thereby forming the piezoelectric element **300** containing a complex oxide, which is a perovskite type complex oxide containing bismuth, iron, and cerium and has a molar ratio of each metal of Bi:La:Ce:Fe=(1−x−y):x:y:1 (the x and y values are as shown in Table 1), as the piezoelectric layer **70**.

Samples 2 to 4

The piezoelectric element **300** was formed in the same manner as in Example 1, except changing the mixing ratios of a xylene solution and an octane solution of 2-ethylhexanoic acid bismuth, 2-ethylhexanoic acid cerium, and 2-ethylhexanoic acid iron and using a complex oxide of Bi:La:Ce:Fe=(1−x−y):x:y:1 (the x and y values are as shown in Table 1) as the piezoelectric layer **70**.

Samples 5 to 22

The piezoelectric element **300** was formed in the same manner as in Example 1, except using a mixture obtained by mixing a xylene solution and an octane solution of 2-ethylhexanoic acid bismuth, 2-ethylhexanoic acid lanthanum, 2-ethylhexanoic acid cerium and 2-ethylhexanoic acid iron at a given ratio, repeating the firing process 4 times in which firing is performed at once after repeating the application process and the drying and degreasing process 3 times, and using a complex oxide of Bi:La:Ce:Fe=(1−x−y):x:y:1 (x and y values are as shown in Table) as the piezoelectric layer **70**.

TABLE

	1 − x − y	X	Y	Ce/(Ce + Bi)	La/ (Ce + Bi + La)
Sample 1	0.99	0.00	0.01	0.01	0.00
Sample 2	0.95	0.00	0.05	0.05	0.00
Sample 3	0.90	0.00	0.10	0.10	0.00
Sample 4 (Comp. Ex.)	1.00	0.00	0.00	0.00	0.00
Sample 5	0.94	0.05	0.01	0.01	0.05
Sample 6	0.90	0.05	0.05	0.05	0.05
Sample 7	0.85	0.05	0.10	0.11	0.05
Sample 8 (Comp. Ex.)	0.90	0.10	0.00	0.00	0.10
Sample 9	0.89	0.10	0.01	0.01	0.10
Sample 10	0.87	0.10	0.03	0.03	0.10
Sample 11	0.85	0.10	0.05	0.06	0.10
Sample 12	0.83	0.10	0.07	0.08	0.10
Sample 13	0.80	0.10	0.10	0.11	0.10
Sample 14 (Comp. Ex.)	0.85	0.15	0.00	0.00	0.15
Sample 15	0.84	0.15	0.01	0.01	0.15
Sample 16	0.82	0.15	0.03	0.04	0.15
Sample 17	0.80	0.15	0.05	0.06	0.15
Sample 18	0.75	0.15	0.10	0.12	0.15
Sample 19	0.79	0.20	0.01	0.01	0.20
Sample 20	0.77	0.20	0.03	0.04	0.20
Sample 21	0.75	0.20	0.05	0.06	0.20
Sample 22	0.70	0.20	0.10	0.13	0.20

Test Example 1

Each of the piezoelectric elements of the samples 1 to 4 was determined for the relationship (P-E curve) between the polarization and electric fields by applying a triangular wave having a frequency of 1 kHz at room temperature using a ϕ=400 μm electrode pattern by "FCE-1A" manufactured by TOYO Corp. The results of the sample 4 (Comparative Example) are illustrated in FIG. **10**A, the results of the sample 1 are illustrated in FIG. **10**B, the results of the sample 2 are illustrated in FIG. **10**C, and the results of the sample 3 are illustrated in FIG. **10**D. As a result, as illustrated in FIGS. **10**A to **10**D, the samples 2 to 4 containing Bi, Fe, and Ce were ferroelectrics. In contrast, the sample 4 (Comparative Example) which is bismuth ferrate and does not contain Ce did not exhibit a favorable hysteresis.

Test Example 2

The piezoelectric elements of the samples 1 to 4 were determined at room temperature for the powder X-ray diffraction pattern of the piezoelectric layer using "D8 Discover" manufactured by Bruker AXS using a CuKα line as the X-ray source. The X ray diffraction patterns showing the correlation between the diffraction intensity-diffraction angle 2 θ are illustrated in FIG. **11**. As illustrated in FIG. **11**, the peak derived from the ABO_3 type structure and the peak derived from the substrate were observed in all the samples 1 to 4. In addition, as illustrated in FIG. **11**, a $Bi_2Fe_4O_9$ heterophase was observed in the samples 1 to 4.

Test Example 3

Each of the piezoelectric elements of samples 1 to 4 was measured for the J-E Curve at room temperature using "4140B" manufactured by Hewlett Packard Co. The results are illustrated in FIG. **12**. In addition, as illustrated in FIG. **12**, the samples 1 to 3 containing Ce exhibited more favorable insulation properties than those of the sample 4 (Comparative Example) not containing Ce.

Test Example 4

The piezoelectric elements of the samples 1 to 3 were determined at room temperature for the relationship of the electric field-induced distortion—the electric field intensity by applying a voltage having a frequency of 1 kHz using a displacement measuring device (DBLI) manufactured by aixACCT GmbH and using a θ=500 μm electrode pattern. The results confirmed that the samples 1 to 3 were displaced. As one example of the results, the results of the sample 1 are illustrated in FIG. **13**.

Test Example 5

Each of the piezoelectric elements of the samples 5 to 22 was determined for the relationship (P-E curve) of the polarization and the electric fields in the same manner as in Test Example 1. As one example of the results, the results of the sample 6 are illustrated in FIG. **14**A, the results of the sample 11 are illustrated in FIG. **14**B, the results of the sample 17 are illustrated in FIG. **14**C, and the results of the sample 21 are illustrated in FIG. **14**D. As illustrated in FIGS. **14**A to **14**D, the samples 6 and 11 were ferroelectrics and the samples 17 and 21 were antiferroelectrics.

Test Example 6

The piezoelectric elements of the samples 5 to 22 were determined for the powder X-ray diffraction pattern of the piezoelectric layer at room temperature using "D8 Discover"

manufactured by Bruker AXS and using a CuKα line as the X-ray source. As one example of the results, the results of the sample 11 are illustrated with the results of the sample 2 in FIG. **15**. The results of the samples 6, 11, and 17 are illustrated in FIGS. **16**A and **16**B. FIG. **16**B is an enlarged view of the principal portion of FIG. **16**A.

As a result, the peak derived from the ABO_3 type structure and the peak derived from the substrate were observed in all the samples 5 to 22 but the $Bi_2Fe_4O_9$ hetero-phase observed in the samples 1 to 4 was suppressed.

In the sample 6, the diffraction peak belonging to a phase (ferroelectric phase) exhibiting ferroelectricity was observed near 2θ=46° as indicated by the arrow a in FIG. **16**B. In the sample 17, the diffraction peak belonging to a phase (antiferroelectric phase) exhibiting antiferroelectricity was observed near 2θ=46.5° C. as indicated by the arrow **13** in FIG. **16**B. In the sample 11, both the diffraction peak belonging to the ferroelectric phase and the diffraction peak belonging to the antiferroelectric phase were observed. This confirmed that the sample 17 was an antiferroelectric and the samples 6 and 11 are ferroelectrics. The sample 11 exhibited the Morphotropic phase boundary (M. P. B.) of the antiferroelectric phase and the ferroelectric phase.

FIG. **17** illustrates a diagram in which the results of analyzing each of the samples 1 to 22 to determine whether the samples were antiferroelectrics or ferroelectrics and further whether or not the samples were ferroelectrics exhibiting the Morphotropic phase boundary from the X ray diffraction patterns are plotted against the composition ratio of La and Ce. As illustrated in FIG. **17**, it was clarified that the piezoelectric elements can become ferroelectrics or antiferroelectrics exhibiting an electric field-induced phase transition depending on the La addition amount or the like.

Test Example 7

Each of the piezoelectric elements of the samples 5 to 22 was measured for the J-E Curve by the same method as in Test Example 3. One example of the results is illustrated in FIGS. **18**A and **18**B. FIG. **18**B is a diagram in which the values at 500 $kVcm^{-1}$ were plotted against the composition ratio of Ce. The results confirmed that, even in the case of the piezoelectric material to which La was further added, the effects of increasing the insulation properties to a high degree and suppressing a leakage current obtained by the Ce addition shown in Test Example 3 above can be maintained as illustrated in FIG. **18**.

Test Example 8

The piezoelectric elements of the samples 5 to 22 were determined for the relationship of the electric field-induced distortion and the voltage at room temperature by applying a voltage having a frequency of 1 kHz using a displacement measuring device (DBLI) manufactured by aixACCT GmbH and using a ϕ=500 μm electrode pattern. As one example of the results, the results of the sample 6 are illustrated in FIG. **19**A, the results of the sample 11 are illustrated in FIG. **19**B, the results of the sample 17 are illustrated in FIG. **19**C, and the results of the sample 21 are illustrated in FIG. **19**D. In FIGS. **19**A to **19**D, the dotted line represents the polarization and the solid line represents the displacement. As a result, the displacement level of the sample 17 and the sample 21 which are antiferroelectrics was high as illustrated in FIGS. **19**A to **19**D. The displacement of the sample 11 which exhibits the Morphotropic phase boundary was higher than that of the sample 6 which is a ferroelectric.

Other Embodiments

As described above, one embodiment of the invention is described but the fundamental structure of the invention is not limited to the above-described embodiments. For example, the silicon single crystal substrate is mentioned as an example of the flow path forming substrate **10** in the embodiments described above but, without particularly being limited thereto, materials, such as an SOI substrate and glass, may be used.

In the embodiments described above, the piezoelectric element **300** in which the first electrode **60**, the piezoelectric layer **70**, and the second electrode **80** are successively laminated on the substrate (flow path forming substrate **10**) is mentioned as an example but the invention is not particularly limited thereto and can also be applied to a longitudinal vibration type piezoelectric element in which a piezoelectric material and an electrode formation material are alternately laminated and which expands and contracts in the axial direction.

Each of the ink jet recording heads of these embodiments constitutes a part of a recording head unit having an ink flow path communicating with an ink cartridge or the like and is mounted on the ink jet recording device. FIG. **20** is a schematic view illustrating one example of the ink jet recording device.

In an ink jet recording device II illustrated in FIG. **20**, cartridges **2**A and **2**B constituting an ink supply member are detachably provided to recording head units **1**A and **1**B having the ink jet recording heads and a carriage **3** carrying the recording head units **1**A and **1**B is provided to a carriage axis **5** attached to a device body **4** in such a manner as to freely move in the axial direction. The recording head units **1**A and **1**B discharge a black ink composition and a color ink composition, respectively, for example.

The carriage **3** carrying the recording head units **1**A and **1**B is moved along the carriage axis **5** by transmission of a driving force of a drive motor **6** to the carriage **3** through two or more gears (not illustrated) and a timing belt **7**. A platen **8** is provided to the device body **4** along the carriage axis **5**, so that a recording sheet S which is a recording medium, such as paper, which is fed by a feed roller (not illustrated) or the like, is wound around the platen **8** and conveyed.

In the embodiments described above, the description is directed to the case where the ink jet recording head is taken as an example of the liquid ejection head. However, the invention is widely directed to general liquid ejection heads and it is a matter of course that the invention can also be applied to liquid ejection heads that ejects liquid other than ink. Examples of other liquid ejection heads include various kinds of recording heads for use in image recording devices, such as a printer, color material ejection heads for use in manufacturing color filters of liquid crystal displays and the like, electrode material ejection heads for use in forming electrodes of an organic EL display, FED (field emission display), and the like, and bioorganic material ejection heads for use in manufacturing bio chips.

The invention is not limited to the piezoelectric elements to be mounted on the liquid ejection heads typified by the ink jet recording head and can also be applied to piezoelectric elements to be mounted on other devices, such as: ultrasonic devices, such as an ultrasonic transmitter, ultrasonic motors, pressure sensors, piezoelectric pumps, and vibration power generation devices that convert a mechanical vibration into electrical power. The invention can also be similarly applied to pyroelectric elements, such as an IR sensor, and ferroelectric elements, such as a ferroelectric memory.

What is claimed is:

1. A piezoelectric element, comprising:

electrodes, and

a piezoelectric layer disposed between the electrodes,

wherein the piezoelectric layer is a ABO_3 perovskite type complex oxide containing bismuth, iron, and cerium, the cerium exists in the A site, and the piezoelectric layer contains the cerium in a proportion of 0.01 molar ratio or more and 0.13 molar ratio or lower based on the total amount of the bismuth and the cerium.

2. The piezoelectric element according to claim **1**, wherein the piezoelectric layer further contains lanthanum.

3. The piezoelectric element according to claim **2**, wherein the piezoelectric layer contains the lanthanum in a proportion of 0.05 molar ratio or more and 0.20 molar ratio or lower based on the total amount of the bismuth, the cerium, and the lanthanum.

4. The piezoelectric element according to claim **2**, wherein the piezoelectric layer exhibits an electric field-induced phase transition.

5. The piezoelectric element according to claim **2**, wherein the piezoelectric layer is a ferroelectric.

6. The piezoelectric element according to claim **1**, wherein, in the piezoelectric layer, a diffraction peak belonging to a phase exhibiting ferroelectricity and a diffraction peak belonging to a phase exhibiting antiferroelectricity are simultaneously observed in a powder X-ray diffraction pattern.

7. A liquid ejection device, comprising the piezoelectric element according to claim **1**.

8. An IR sensor, comprising the piezoelectric element according to claim **1**.

9. An ultrasonic device, comprising the piezoelectric element according to claim **1**.

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